

# SORPTION OF MERCURY (II) ON COAL IMPREGNATED WITH OXIDES OF MANGANESE

*A thesis submitted*

in Partial Fulfilment of the Requirements  
for the degree of

MASTER OF TECHNOLOGY

*by*

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*to the*

DEPARTMENT OF CIVIL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
AUGUST, 1984

To

Amma, Nanna,  
SriDevi, Pramada  
and  
Srinivas.

22 AUG 1984

U. S. DEPARTMENT OF JUSTICE

FEDERAL BUREAU OF INVESTIGATION

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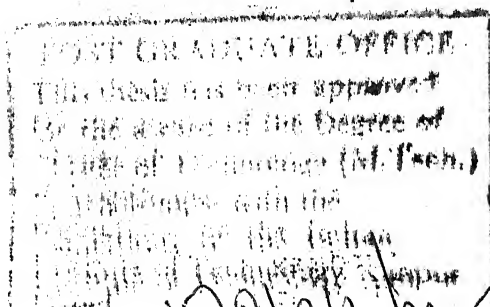
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CERTIFICATE

Certified that the work presented in this thesis entitled "Sorption of Mercury(II) on Coal Impregnated with Oxides of Manganese" by Sri T.V. Kiran. Kumar has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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## ACKNOWLEDGEMENTS

I am indeed grateful to my mentor, Dr. Malay Chaudhuri whose excellent guidance and constant encouragement have led to the successful completion of this work. I wish I have a source of inspiration as good as him for all times to come.

I am deeply indebted to Dr. A.V.S. Prabhakara Rao, Dr. C. Venkobachar, Dr. Vinod Tare and Dr. (Mrs.) Leela Iyengar for their copious advice and stimulating discussions.

I wish to record my deep sense of gratitude to Dr. S. Sarkar, Dr. T.R. Ramachandran, Dr. S.K. Gupta and Dr. U.S. Mehrotra for sparing their valuable time whenever I approached, despite their busy schedule.

I remember Dr. (Miss) M.R. Sharma's timely help in arranging mercury analyser for my use without which this work would not have been completed in time. My sincere thanks to her. I am thankful to Sri E.S. Jadon for permitting me to use mercury analyser. Also, I wish to express my thanks to the staff, U.P. Pollution Control Board for its cooperation during my experimental work in their laboratory.

I sincerely appreciate the help rendered by Sri R.C. Adhikari. I duly acknowledge the help received from Messrs. Hasan, N.R. Sahu, S.N. Mishra, Vijay Bahadur and Indradeo.

I am thankful to Messrs. M.N. Mungole, V.P. Sharma and Sairam for their technical assistance. I wish to express my sincere thanks to Miss. Uma Devi for her help in operating vacuum system.

I am very much thankful to my fellow research scholars who made my stay at Kanpur enjoyable, Messrs. S.C. Prasad, V.S. Prasad, A.K. Dutta, Venkat, Ahmad, Amitabh, A.K. Jain, Bhuwan, Chakraborty, Kandasamy, Sarat, Sanjeev, Satyanarayana, Uday Bhaskar and Misses Rashmi and Suchita for their cooperation and help. I sincerely thank my friends, Manoj, Rama Kant, Sen Gupta, Sitaramam, Subba Rao and Venu for their help.

A word of praise for Sri R.N. Srivastava and Sri V.P. Gupta for excellent typing and drawing.

Finally, . . . well, what can I write (It's beyond my expression) for the love and affection of the families of Dr. C. Venkobachar and Sri A.K. Jain.

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## 1. INTRODUCTION

Although water appears to be a vast renewable resource, its future is troubled by the same problem that plagues so many other natural resources — a growing population making demands on a finite supply. The flow of water is not increasing in proportion to population growth. Nature's rate of cycling of water through the ecosystem sets a fixed limit on the amount of water that can be diverted from natural flows for human use. In many regions, that limit is being rapidly approached. Yet, water is perhaps man's most important resource.

The quality of this finite resource deteriorates with the diurnal activities of human beings, thereby, effecting a depletion in the usable quantity. To banish the spectre of the world without water, scientists are working on ways to reuse this fast depleting natural resource. Evidently, as reuse practice increases more stringent regulations will be laid on the treatment of water and wastewater.

The ubiquity of heavy metals in industrial processes is significantly responsible for the deterioration of water quality. Mercury contamination of drinking water by discharges of mercury-laden industrial wastes is now recognised as a potential danger since its presence in the aquatic environment has been known to cause severe health problems to animals and human beings. Hence, the concentration of mercury in drinking water supplies must be

extremely low. The following standards have been set in view of the high toxicity of mercury:

WHO International Drinking Water Standard (1971)	0.001 mg/l
Government of India Drinking Water Standard (Manual on Water Supply and Treatment, 1976)	0.001 mg/l
Tolerance limit for industrial effluents discharged into inland surface waters (IS:2490 (Part I) - 1981)	0.01 mg/l
Threshold Limit Value (TLV) in air for repeated exposure for 8 hours work day and 40 hours work week (IS:7812-1975)	0.05 mg/m <sup>3</sup>

Among the many methods, viz., sulfide precipitation, alum coagulation, iron coagulation, ion exchange, lime softening and activated carbon adsorption suggested for the mercury removal, the activated carbon adsorption process appears particularly competitive and effective in the removal of mercury at trace quantities (Patterson, 1975). However, the technology to produce good quality of activated carbon is often beyond the reach of many developing nations. Besides this, cost of production and effective regeneration of activated carbon is very high. In general, adsorption of heavy metals on hydrous manganese dioxide and some locally available low cost materials, viz., coal, coconut shell and rice husk is of interest to many researchers in recent times. Research is also being done to enhance the sorption capacity of the low cost materials through chemical pretreatment. Karthikeyan (1982) included manganese treated coal in his study on mercury sorption but did not conduct a detailed investigation.

In the present study an attempt was made to investigate in details the enhancement of mercury(II) sorption by coal through impregnation of the various oxides of manganese. The study was conducted in the laboratory in two phases, viz., sorbent characterisation and batch sorption tests to evaluate the effect of chemical pretreatment on mercury sorption.

## 2. PRESENT STATE OF KNOWLEDGE

### 2.1 Mercury

#### 2.1.1 General

Mercury is a naturally occurring element, belonging to Group IIB of the periodic table, that is found in minerals, rocks, soil, water, air, plants and animals. Commonly called "quick silver" because of its bright metallic appearance and dry-liquid consistency, it is the only metal (and the only element besides bromine) that is liquid at ordinary room temperatures. As a consequence the vapour pressure of mercury in its elemental state is substantial even at ambient temperatures. In nature mercury can be found in any of the three different oxidation states: elemental (0), mercurous (+1) and mercuric (+2).

#### 2.1.2 Properties of Mercury

A few important properties of mercury are listed below (Schroeder, 1982 and IS:7812-1975).

Atomic number	80
Atomic weight	200.61
Melting point	-38.9°C
Boiling point	356.9°C
Density	13.546 gm/cm <sup>3</sup> at 20°C
Vapour pressure	0.246 pa at 25°C
Description	Silvery white liquid metal



### Solubility:

- a) in water                      Sparingly soluble (64 µg/l at 25°C)
  - b) in acids                      Soluble in dilute nitric acid
- Reactivity                      Readily reacts with halogens, sulphur,  
conc. HCl, conc. H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>S, etc.

### 2.1.3 Uses of Mercury

The major consumptive user of mercury is the chlor-alkali industry. Mercury is widely used in amalgams, scientific instruments, batteries, arc lamps, the extraction of gold and silver. Its salts are used as fumigants in combating plant diseases and insect pests. It is also used as an antifoulant in ship paints and mildew-proofing of canvas tarpaulins and tents. Besides these, mercury is also used in the electronics industry, detonators manufacturing, photographic industry, textile industry, ink manufacturing, leather tanning, paper mills, glassware manufacturing and preservative industry. Mercury is used as a catalyst in the chemical and petrochemical industry.

Organomercurials, like phenyl mercuric acetate and methyl mercury, are used mostly as fungicides, bactericides and slimicides. Mercury is also found in most laboratory wastewaters. Power generation is a large source of mercury release into the environment through combustion of fossil fuel.

In addition to the practical application and utilisation of mercury-based technology, there are many experimental applications of mercury in rather exotic uses. For example, the use of mercury has been proposed for liquid

fly-wheels and gyroscopes for spacecraft stabilisation, ion engines for rockets, nuclear-reactor coolants, fuel cells and turboelectric power systems.

## 2.2 Mercury in the Environment

Mercury is widely distributed in nature, almost always in quite low concentrations; mercury as a contaminant enters the environment at only a few locations, but in relatively large amounts. As a result of man's utilisation and exploitation of mercury and mercury-based technology, many forms of mercury are being released into the environment.

Mercury is widely distributed in rocks and minerals; as the metal in small amounts; as the amalgams with Au, Ag and the platinum metals; as sulfides, selenides and a telluride; as oxide, oxychloride and complex hydrous chloride-sulfates. The main ore is cinnabar ( $\text{Hg}_2\text{S}$ ) from which mercury is extracted by roasting in a current of air. The terrestrial abundance of mercury in rocks is in the range of 2 to 3000 ppb (Liptak, 1974). Gavis and Ferguson (1972) estimated that in the year 1970 about 3300 tonnes of mercury from ores were released into the atmosphere. According to them about 800 tonnes of mercury <sup>per year</sup> are released into the atmosphere by rock weathering.

The normal concentration of mercury in soils is 20 to 150 ppb, average 70 ppb, except near mercury deposits where it may go upto 250 ppb. The mercury content of natural waters is 0.2 ppb in rain water; 0.3 ppb in normal streams, rivers and lakes; 0.05 ppb in normal ground waters and 0.2 ppb in oceans and seas. Waters near mercury and sulfide

deposits and hot springs may have mercury levels upto 1000 ppb. The mercury content of the atmosphere, expressed in nanograms per cubic metre, is 2 to 10, with higher values in industrial areas and 0.5 over oceans. It is highly variable, 3 to 1600 ng per cubic metre over mercury deposits and even higher in areas with volcanic exhalations (Liptak, 1974).

Heindryckx et al. (1974) calculated the amount of mercury released into the environment and gave the following figures.

Combustion of coal and lignite: 300 T/yr  
Refining and combustion of petroleum and natural gas: 400 T/yr  
Production of steel, cement and phosphate: 500 T/yr

Korringa and Hagel (1974) have calculated the annual amount of mercury reaching the earth's surface due to precipitation of rainfall and arrived at a figure approximately 30000 tonnes.

D'Itri (1972) estimates that 180-360 kg of mercury per year per million urban population may be released through sewage into the environment as a result of incidental uses of mercury-containing compounds by individuals and businesses like water-based paints, paper products, cosmetics, broken thermometers, discarded pharmaceuticals etc. It is further pointed out that sewage sludge can retain high amounts of mercury (6-20 mg/kg). This sludge is sometimes used as a fertiliser resulting in widespread disposal of mercury or is sometimes burnt in multiple hearth furnaces when most of the mercury would probably be released into the atmosphere.

Komerwar et al. (1978) estimated that in India during 1976 about 90.8 tonnes of mercury was released into atmosphere by the chlor-alkali industries. The concentration of mercury in the Ganga river water near Kanpur was reported to be 0.3 ppb (Dutt and Chaudhuri, 1980). The Hooghly estuary showed a minimum concentration of 0.7 ppb at Serampore (NEERI Report, 1980). The reported level of mercury in a few samples of fish from the Bombay coast was 500 ng/g (Tejam and Haldar, 1975). Ayyadurai et al. (1983) reported that water samples collected from twelve spots in Madras city showed a concentration range of 2.43-32.99 ng/ml. The concentration of mercury in Rihand reservoir was reported to be in the range of 2-4  $\mu\text{g/l}$  (Sharma, 1984). These figures indicate that mercury pollution has not yet reached alarming proportions in India and any further addition to the existing level may pose a threat. Hence, all efforts should be made to preserve the aquatic environment and other natural ecological systems.

### 2.3 Chemistry of Mercury in Aqueous Solutions

Natural waters and their environs are complex heterogeneous electrolyte systems containing both organic and inorganic matter. It is doubtful whether any attempt to describe these complex systems in full detail will ever be complete. However, one can gain useful insights into the chemistry of natural waters by application of equilibrium models to simple heterogeneous and homogeneous systems. To improve agreement between equilibrium models and natural

water behaviour, nonequilibrium kinetic models need to be developed (Leckie and James, 1974).

Natural waters are electrolyte solutions in contact with solids of macroscopic to colloidal dimensions. In addition to simple ion-ion interactions, there will also be ion-solvent, ion-solid, and solvent-solid interactions that may be important in the distribution and transport of metal ions between the solid and aqueous phases. The solubility of minerals and coordinative compounds of metal ions is perhaps the most important phenomenon responsible for the presence of trace metals in natural waters. The important parameters controlling the solubility of mineral phases are the pH of solution, the type and concentration of complexing inorganic and organic ligands and chelating agents, the oxidation state of the mineral components, and the redox environment of the system (Leckie and James, 1974).

Mercury can be present in one or more of the three different oxidation states under the usual conditions of temperature that occur in river and lake water and water saturated sediments. The most reduced, in a chemical sense, of these forms is the mercury metal, which is a liquid at ordinary temperature. The other two forms are ionic; the more reduced of the two ions is the mercurous ( $\text{Hg}_2^{++}$ ). In oxidising conditions, especially at low pH, the stable form is the mercury(II) ion ( $\text{Hg}^{++}$ ).

Mercury(II) is well known for its ability to form stable complexes with inorganic ligands. Although bonding through oxygen is weaker than sulphur or nitrogen, it is

strongly hydrolysed compared to most divalent metal ions. A set of data for the hydrolysis, chosen from Sillen and Martell (1964), is given in Table 1. The maximum concentration of  $\text{Hg}(\text{OH})_2^0$  is much higher than the solubility of most divalent heavy metal hydroxides.

Some ligands that form soluble complex ions and molecules can also react in another way by dissolving other insoluble phases. For example, mercuric ions form very stable complexes with chloride ions (e.g.,  $\text{HgCl}^+$ ,  $\text{HgCl}_2^0$ ,  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{=}$ ) while the  $\text{HgCl}_2(\text{s})$  phase remains quite soluble. In chloride-free solutions, mercuric ions hydrolyse at low pH ( $\approx 3$ ) and may form a solid precipitate  $\text{HgO}(\text{s})$ , if the concentration is greater than 50 ppm ( $\approx 2.5 \times 10^{-4}$  mol/l). However, in presence of excess chloride ion, say  $10^{-3}$  M, the  $\text{Hg}^{++}$  reacts to form  $\text{HgCl}_2^0$ , thus decreasing free  $\text{Hg}^{2+}$  so that hydrolysis products only become dominant at higher pH values (pH 6  $\sim$  7). Therefore, complexation by one kind of ligand ion results in the increased metal ion solubility of the precipitate of another ligand (Leckie and James, 1974).

Mercury(II) forms strong complexes with halides in the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . The stability constants for chloro complexes are also given in Table 1. Reimers et al. (1974) gave a table showing the species distribution of the inorganic forms of mercury under different conditions of chloride concentrations and pH (Table 2).

Table 1

Solubility and Complex Formation Equilibria for Mercury  
(Sillen and Martell, 1964)

Equilibria	log K (25°C)
1. Solubility equilibria	
$\text{HgO(s)} + \text{H}_2\text{O} = \text{Hg(OH)}_2(\text{aq})$	-3.7
$\text{HgO(s)} + \text{H}_2\text{O} = \text{Hg}^{2+} + 2\text{OH}^-$	-25.7
$\text{Hg(l)} = \text{Hg(aq)}$	-6.50
$\text{HgCl}_2(\text{s}) = \text{Hg}^{2+} + 2\text{Cl}^-$	-13.8
$\text{Hg}_2\text{Cl}_2(\text{s}) = \text{Hg}_2^{2+} + 2\text{Cl}^-$	-18.00
2. Complex formation equilibria	
$\text{Hg}^{2+} + \text{H}_2\text{O} = \text{HgOH}^+ + \text{H}^+$	-3.4
$\text{Hg}^{2+} + 2\text{H}_2\text{O} = \text{Hg(OH)}_2^0 + 2\text{H}^+$	-6.00
$\text{Hg}^{2+} + 3\text{H}_2\text{O} = \text{Hg(OH)}_3^- + 3\text{H}^+$	-20.7
$\text{Hg}^{2+} + \text{Cl}^- = \text{HgCl}^+$	6.7
$\text{Hg}^{2+} + 2\text{Cl}^- = \text{HgCl}_2^0$	13.2
$\text{Hg}^{2+} + 3\text{Cl}^- = \text{HgCl}_3^-$	14.2
$\text{Hg}^{2+} + 4\text{Cl}^- = \text{HgCl}_4^{2-}$	15.2
$\text{HgCl}_2^0 + \text{H}_2\text{O} = \text{HgOHCl}^0 + \text{Cl}^- + \text{H}^+$	-9.6
$\text{HgCl}_2 + 2\text{H}_2\text{O} = \text{Hg(OH)}_2^0 + 2\text{Cl}^- + 2\text{H}^+$	-19.6

Model parameters:  $r_{\text{Hg}^{++}} = 1.1 \text{ \AA}$ ,  $r_{\text{H}_2\text{O}} = 1.38 \text{ \AA}$ .  
Area per Hg(II) complex =  $50 \text{ \AA}^2$ .

Table 2

Species Distribution of the Inorganic Mercury Under Different Conditions of Chloride Concentrations and pH  
(Reimers et al., 1974)

Chloride concentration	Species of inorganic mercury		
	pH 5.0	pH 7.0	pH 9.0
18000 ppm	$\text{HgCl}_4^{=}$	$\text{HgCl}_4^{=}$	$\text{HgO} \cdot \text{H}_2\text{O}$
10000 ppm	$\text{HgCl}_4^{=}$	$\text{HgCl}_4^{=}$	$\text{HgO} \cdot \text{H}_2\text{O}$
100 ppm	$\text{HgCl}_2$	$\text{HgO} \cdot \text{H}_2\text{O}$	$\text{HgO} \cdot \text{H}_2\text{O}$

The log concentration -pH diagrams for the chloro, hydroxo-chloro complexes are shown in Figures 1 and 2 for the equilibrium chloride concentrations of  $10^{-1}$  M and  $10^{-3}$  M, and a total Hg(II) concentration of  $10^{-7}$  M (Butler, 1964). From these figures it can be seen that over the concentration range  $[\text{Cl}^-] = 0$  to  $10^{-1}$  M and between pH 3 and 14, the predominant soluble mercury(II) species is either  $\text{Hg}(\text{OH})_2^0$  or  $\text{HgCl}_2^0$ . As the chloride concentration is increased from 0 through  $10^{-3}$  to  $10^{-1}$ ,  $\text{Hg}(\text{OH})_2^0$  becomes predominant at pH 3, 6.8, and 8.8.

In solutions of Hg(II) and chloride ions, where the molar ratio of chloride to mercury is two, the only species will be  $\text{Hg}^{++}$ ,  $\text{HgCl}^+$ ,  $\text{HgCl}_2$  and  $\text{Hg}(\text{OH})_2$  (Marcus, 1965). When there is an excess of free chloride ion, the complexes  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{=}$  are formed in addition to the above species. This chloride interference decreases at higher pH as  $\text{Cl}^-$  is



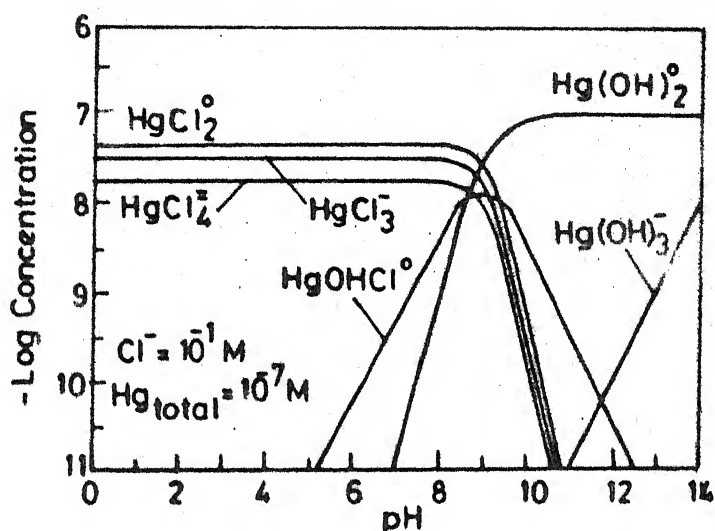


Fig. 1

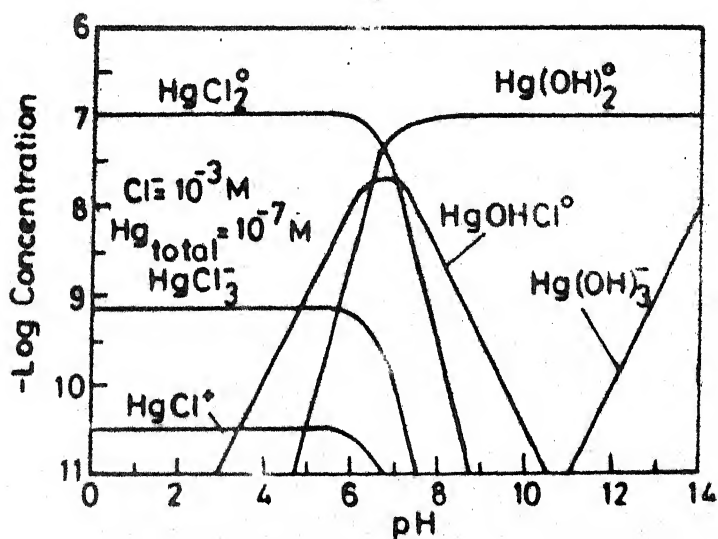


Fig. 2

Fig. 1 & 2. Log Concentration pH Diagram for Mercury at 25°C (Rubin, 1973)

Fig. 1 :  $10^{-7} \text{ M}$  Total Mercury and  $10^{-1} \text{ M}$  Total Chloride.

Fig. 2 :  $10^{-7} \text{ M}$  Total Mercury and  $10^{-3} \text{ M}$  Total

replaced by  $\text{OH}^-$  (Masri and Friedman, 1973). All of these forms of ionic mercury exist in equilibrium with each other.

It appears that mercury(II) exhibits the general sorption properties of hydrolysable metals, e.g., the strong pH dependence of sorption. The fraction sorbed increases abruptly at different pH values depending upon the chloride concentration. Quantitatively, the pH range of the abrupt increase corresponds to the pH range over which  $\text{Hg}(\text{OH})_2^0$  assumes dominance over  $\text{HgCl}_2^0$ . This behaviour is summarised in Table 3. It can be inferred from these observations that  $\text{Hg}^{++}$  and the  $\text{Hg}(\text{II})\text{-Cl}^-$  complexes are either not adsorbed at all or are only weakly adsorbed in comparison to the hydroxo complexes of Hg(II).

Inorganic ligands found in natural waters with strong affinities for  $\text{Hg}^{++}$  ion seem to be numerous. It is interesting to note that metal ions normally found in natural waters are associated with hydrous oxides, clays and biological

Table 3

Adsorption of Hydrolysis Products of Hg(II) on  $\text{SiO}_2$   
(James and Healy, 1972)

$\text{Cl}^- \text{ M}$	pH range of abrupt adsorption increase	pH at which $\text{Hg}(\text{OH})_2^0$ becomes predominant
0	2-3	3.0 $\text{Hg}^{++} = \text{Hg}(\text{OH})_2^0$
$10^{-3}$	6-7	6.8 $\text{HgCl}_2^0 = \text{Hg}(\text{OH})_2^0$
$10^{-1}$	8-9	8.8 $\text{HgCl}_2^0 = \text{Hg}(\text{OH})_2^0$

organic matter. Apparently, mercury discharged into receiving waters may be transformed chemically, physically and/or biologically under appropriate conditions, undergo sorption and/or surface complexation on inorganic or organic sorbents and subsequently ingested by living organisms.

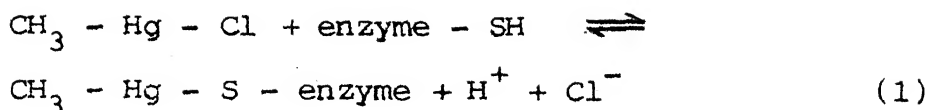
#### 2.4 Toxicity and Biological Effects of Mercury

The most spectacular incident of mercury poisoning resulted from the ingestion of sea food taken from Minamata Bay, Japan, during the late 1950's. The Chisso Chemical Company constructed a plastics plant which used organomercurials as catalysts, and each year a small quantity of chloromethyl mercury(II) was discharged into the Minamata Bay. Beginning in 1953 a strange illness affected the people of Minamata - they became tired, irritable, complained of headaches, numbness in arms and legs and difficulty in swallowing and began to experience blurring of vision, loss of hearing and muscular coordination, inflammation of gums, and a metallic taste in their mouths. Since the cause of these symptoms was not evident they came to be known as "Minamata disease". By 1963 it had been determined that the disease was caused by mercury (at levels between 27 and 102 ppm dry weight) in the staple food of the community-fish taken from the bay. Of a total of 111 cases reported, 43 died. Babies born of afflicted mothers suffered congenital defects. Tragically other similar episodes occurred in the Guatemalan Highlands in 1965, Pakistan in 1961, Central Iraq in 1961 and Sweden in 1969.

Certain compounds of mercury, of which chloromethyl mercury(II) is an excellent example, tend to concentrate along ecological food chains, a process known as "bioamplification". Any substance which is slightly more soluble in the tissues of simple organisms than in the surrounding water will be a more concentrated component of the diet of the more complex species which feed on the simple ones. Thus, at each higher trophic level in the food chain the substance becomes more concentrated. Since human beings are usually at the top of the food chains, high concentrations of poisonous substances may occur in human diets (Moore and Moore, 1976).

Mercury is known as "systemic poison" since it causes damage to various systems of the body. Uptake of mercury can be by inhalation, ingestion, absorption through skin and it is excreted through urine, feces and milk. Cell membrane is the first site of attack as it contains sulfhydryl groups which are known to have a very high affinity for mercury compounds (Rothstein, 1973). Almost all proteins contain sulfhydryl groups and thus every protein in the body is a potential target.

Once in the human body organomercurials and divalent mercury both react with a large number of enzymes, usually inhibiting catalysis of essential metabolic reactions. This apparently results from the strong bonds formed between the large, soft  $\text{Hg}^{2+}$  ion and sulfhydryl ( $-\text{SH}$ ) groups on the amino acid cysteine in the enzymes:



The mercury-containing group can disrupt the enzyme's structure and consequently impeding its catalytic function (Moore and Moore, 1976).

The acute toxicity may usually be due to ingestion of large amounts of inorganic mercury compounds or from exposure to high dose of organic mercury compounds. Acute systemic effects may be due to damage to kidneys. The possible symptoms of exposure may be metallic taste, salivation, burning, swelling, abdominal pain, diarrhoea, ulceration and intestinal haemorrhage. Many symptoms suddenly become acute leading to circulatory damage. Acute local effects may produce irritation, vesication and corrosion of the skin. This may lead to a dermatitis or eczematic rash. Chronic exposure to mercury causes damage to the nervous system. Chronic effects include: psychic disturbances, erethism, stomatitis, tremor, salivation, gingivitis. Weakness, fatigue, weight loss are non-specific symptoms.

## 2.5 Removal of Mercury from Water and Wastewater

Many types of mercury treatment technology have been described in the literature. The effectiveness, and economics of treatment of each type depend upon the chemical nature and initial concentration of mercury, the presence of other constituents in water and wastewater that may interfere with the specific treatment, and the degree of mercury removal that must be achieved. Among the more

common types of treatment are precipitation, ion exchange, adsorption and coagulation, reduction of ionic mercury to elemental form and removal by filtration (Patterson, 1975).

Sulfide addition to precipitate highly insoluble mercury sulfide is the most common precipitation treatment. For high initial mercury levels, sulfide precipitation will achieve 99.9+% removal at alkaline pH, but even with filtration or activated carbon-polishing treatment, minimum effluent mercury achievable appears to be 10-20  $\mu\text{g/l}$ . In addition to lack of capability to reduce mercury below 10  $\mu\text{g/l}$ , other drawbacks include: 1) the formation of soluble mercury sulfide complexes at high levels of excess sulfide, 2) the difficulty of monitoring excess sulfide levels, and 3) the problem of toxic sulfide residual in the treated effluent (Perry, 1974).

Removal of inorganic mercury and organic mercury by coagulation employing alum, iron salts and lime as coagulants was studied by many researchers (Gary et al., 1973; Logsdon and Symons, 1973; and O'Connor, 1974). It was found that in the turbidity range of 10-100 JTU, alum removed 10-60 percent of inorganic mercury while removal of methyl mercury was less under similar conditions. Ferric sulfate removed 40-60 percent of inorganic mercury and low quantities of methyl mercury. It was also found that increasing coagulant dosage to 100-150 mg/l did not improve mercury removal. Mercury removal during coagulation was related mainly to adsorption of mercury onto the turbid-causing agents in the water. Effluent levels of mercury achieved by alum

treatment range from 1.5-102  $\mu\text{g/l}$ , and by iron treatment from 0.5 to 12.8  $\mu\text{g/l}$ .

Logsdon and Symons (1973) also observed about 20-85 percent inorganic mercury removal and 20-70 percent methyl mercury removal by centrifuging the various turbid waters (20-300 JTU) followed by clarification, without coagulation. Removal of mercury during filtration through conventional sand media did not remove any appreciable quantity of mercury and it is reported that the capacity of sand to remove mercury is limited.

In softening processes mercury removal was pH dependent and 30 percent removal was obtained at pH 9.4 while at pH 10.6-11.0, 60-80 percent removal of inorganic mercury was obtained. Removal of methyl mercury was insignificant in the pH range of 9.4-11.6 (Logsdon and Symons, 1973).

Inorganic ionic mercury can be converted to the metallic form by reduction and separated by filtration or other solids separation techniques. A variety of reducing agents are available, including aluminium, zinc, hydrazine, stannous chloride and sodium borohydride. The main advantage claimed for reduction is that mercury can be recovered, in the metallic state. The data available on mercury removal by reduction process indicate that reduction process cannot effectively achieve mercury levels below 100  $\mu\text{g/l}$  (Patterson, 1975).

Most ion exchange treatment of inorganic mercury involves formation of a negatively charged mercuric chloride complex by addition of chlorine (to oxidise metallic mercury)

or chloride salts, and removal of the mercuric chloride complex on an anion exchange resin. In wastes where chloride is not high, cation exchange resins are effective. Regardless of whether anionic resins are used for mercuric chloride complex removal or cationic resins for mercuric ion removal, best ion exchange treatment for inorganic mercury appears to yield an effluent of 1-5  $\mu\text{g/l}$ . Most effective treatment results from two-stage treatment at neutral to slightly acidic pH (Patterson, 1975).

Among the many methods available for treatment of mercury, sorption appears to be effective and competitive. Many investigations on the sorption of mercury in soils, sediments and rocks have been conducted by geologists and agriculturists (Fleischer, 1970; Jonason, 1970; and Klusman and Matoske, 1983). Adsorption on activated carbon has been of interest to many workers (Humenick and Schnoor, 1974; Logsdon and Symons, 1973; Sigworth and Smith, 1972; Smith et al., 1971; Wehman, 1972; and Huang and Blackenship, 1984). Sands, clays, organics, minerals, alloys, nylons, polyesters, polypropylene, agricultural products, wools, chicken feathers, milk proteins, hair, waste rubber tyre etc. were also used as adsorbents for mercury (Friedman et al., 1971; Reimers and Krankel, 1972; Feick et al., 1972; Tratnyek, 1972; Friedman and Weiss, 1972; McKaveney et al., 1972; Michelsen et al., 1975; Knocke and Hemphill, 1981; and Rowley et al., 1984). Pandey and Chaudhuri (1980) studied mercury removal by bituminous coal. Pandey and Chaudhuri (1982) and Karthikeyan (1982) showed that the sorption



capacity of bituminous coal could be enhanced through chemical pretreatment, viz., nitric acid oxidation, carbon disulfide, hydrogen peroxide and manganese chloride treatment. It appears that adsorption process is effective and competitive for removal of mercury over wide concentration ranges.

A variety of other treatment processes are mentioned in the technical literature, although treatment efficiency data are limited. These processes include solvent extraction with high molecular weight amines, use of silicon alloys for reduction of elemental mercury, removal by starch xanthate-cationic polymer complexation, and various other proprietary processes. Although several of the processes appear promising, they are all in the experimental stages and have not been proved in pilot or full-scale application (Patterson, 1975).

## 2.6 Coal and Its Use in Water and Wastewater Treatment

Coal may be defined as a compact stratified mass of mummified plants which have been modified chemically in varying degree, interspersed with smaller amounts of inorganic matter (Francis, 1950). The greater the portion of carbon content, the higher the rank of the coal. Increase in rank denotes natural process whereby carbon content is increased at the cost of hydrogen and oxygen content. Graphite is the ultimate evolved form of coal and can be considered as the basic structural unit.

The sorption characteristics of sorbents based on carbon, such as graphites, carbon black and activated carbon,

result from a number of crystalline and chemical properties. These involve the structure and dimension of carbon crystallites in the sorbent skeleton, the presence of chemical compounds (mainly containing oxygen and hydrogen either inside the sorbent structure or partially on its surface) as well as the presence or absence of roughness on the surface and porosity (Avgul and Kiselev, 1970). For different deposits of brown coal Cullen and Siviour (1982) report natural moisture contents ranging from 30 to 67 percent, indicating that the coals contain extensive porosity and consequently a large internal surface area which facilitates access to functional groups.

Charcoals and activated carbon are composed of crystals of microscopic dimensions called microcrystallites. Although the microcrystallites have structural resemblance to a large graphite crystal, they differ in many ways such as interlayer spacing and stacking sequence (Hassler, 1963; and Smisek and Cerney, 1970). The interatomic distance between the carbon atoms in the individual layer plane is  $1.42 \text{ \AA}$ . The layer planes are in parallel array with an interlayer spacing of  $3.35 \text{ \AA}$  interbonded by weak van der Waals forces.

The carbon atom is tetravalent and three of the four atoms in the rectilinear hexahedrons forming the layer are firmly bound with three neighbouring atoms by three covalent bonds ( $\sigma$  bonds). The fourth electron of each carbon atom (giving each carbon-carbon bond a one-third double bond character) participates in a  $\pi$ -bond, which is formed by side-to-side overlap of the two orbitals (Hassler, 1963; and

Coughlin and Tang, 1968). The free valences are very reactive and form compounds with suitable foreign atoms easily.

In carbons, the fraction which exists in the form of disordered, single, unstacked graphite-like layers is more susceptible to chemisorption of gases and vapours, while the fraction showing some degree of well-ordered stacking is less susceptible to chemisorption of gases (Puri, 1970). Exposed defects, dislocations and discontinuities in the layer planes of microcrystalline carbons give rise to what are called "active sites" and these are associated with high concentrations of unpaired electron spin center and, therefore, are expected to play a significant role in sorption (Puri, 1970). Edges of microcrystalline are very reactive as has been estimated by Henning (1961) that the edge atoms were atleast 20 times as reactive as atoms within the basal plane. Surface carbon atoms located at "active sites", due to residual valencies, show a strong tendency to chemisorb other elements like oxygen, hydrogen, chlorine, sulfur, etc., and give rise to surface complexes (Puri, 1970). Many of the reactions of charcoals arise either because of the existence of a superficial layer of the chemically bound elements.

Oxygen is chemisorbed more readily than any other element, and oxygen-carbon complexes are by far the most important in influencing surface reactions, surface behaviour, wettability and electrical and catalytic properties of carbon. These complexes are the source of the property by which a carbon becomes useful or effective in certain

respects. These complexes reduce ~~the~~ hydrophobicity and impart a polar character to carbons which leads to preferential sorption. Hydrogen is invariably present in all coals as chemisorbed water, and as hydroxyl, hydroquinonic and possibly carboxyl groups. Although hydrogen is present in small quantities ( $\approx 5\%$ ), seemingly it has considerable influence on the properties of coals (Puri, 1970). The other elements that are usually present in coals include sulfur, nitrogen, etc.

Functional groups formed by oxidation makes the carbon hydrophilic. The most common groups identified by various techniques (spectroscopic, potentiometric and polarographic) are carboxyl, hydroxyl, and phenolic and carboxyl. Other possible groups include lactones, quinoids, aldehydes, hydroquinones and ethereal structures. A characteristic of low rank coals and peats is that much of the oxygen associated with their structure is present as carboxyl groups imparting ion exchange properties (Schafer, 1970). Hydrogen bonding by protons with oxygen is one of the surface interactions (Mattson et al., 1970). Carboxylic and phenolic groups have been repeatedly reported as the major acidic surface oxides.

Coal has been widely used in water and wastewater treatment. In the United States, anthracite coals have long been used in water treatment as filter media. Due to lack of good quality anthracite reserve in India, bituminous coals were evaluated as substitute for anthracite in dual-media filtration (Paramasivam and Deshpandey, 1972).

Ranade (1976) was able to improve the filtration rate by converting a rapid sand filter to a dual-media coal-sand filter without any significant deterioration of water quality. Pandey (1978), Karthikeyan (1982) studied the removal of mercury from water by sorption on raw and chemically treated coal with varying degrees of success. Bhattacharya (1983) and Jayasimha (1983) studied the removal of cadmium and humic acid, respectively, from water by sorption on raw and chemically treated coal.

## 2.7 The System $\text{Mn-O}_2\text{-H}_2\text{O}$

Manganese, atomic number 25, is the fifth of the first transition series of elements. Like the other transition elements, manganese can exist in a number of oxidation states, examples of which range from -3 to +7 (Cotton and Wilkinson, 1962). The aqueous chemistry of manganese involves primarily 2+, 3+, 4+, 6+, 7+ oxidation states. Oxidation states 2+ and 4+ are the lowest and highest that have been observed in natural waters, although the ephemeral existence of other states is conceivable. Commonly, manganese oxide minerals contain more than one oxidation state of manganese. It remains a moot question whether 3+ oxidation state actually occurs or is realised through an equal distribution of 2+ and 4+ states (Bricker, 1965).

Among the various oxides, hydroxides and hydrous oxides of manganese,  $\text{Mn(OH)}_2$ ,  $\text{Mn}_3\text{O}_4$ ,  $\gamma\text{Mn}_2\text{O}_3$ ,  $\gamma\text{MnOOH}$ ,  $\gamma\text{MnO}_2$ ,  $\delta\text{MnO}_2$  and hydrohausmannite are of significant importance in the system  $\text{Mn-O}_2\text{-H}_2\text{O}$ . Various procedures are available for preparing each of these compounds. These compounds are

characterised by the oxidation grade of manganese (by determining oxygen to manganese ratio), X-ray diffraction patterns and/or electron micrographs. A brief review of the preparation procedures available for each of the seven compounds mentioned above follows:

1.  $\text{Mn}(\text{OH})_2$ :

"Pyrochroite" is the mineral name for this compound. De Schulten (1887) prepared  $\text{Mn}(\text{OH})_2$  by treating a manganous chloride solution with concentrated alkali hydroxide under a hydrogen atmosphere. He obtained crystals of 0.2 mm in diameter by redissolving the precipitate in its mother liquor at elevated temperature and cooling slowly. Klingsberg (1958) prepared  $\text{Mn}(\text{OH})_2$  by subjecting manganese metal to 200 psi of water pressure at 363°C for one day. He found that the transition  $\text{MnO} \rightleftharpoons \text{Mn}(\text{OH})_2$  could be made to proceed reversibly at elevated temperature by varying the water pressure. Bricker (1965) precipitated  $\text{Mn}(\text{OH})_2$  from dilute manganous nitrate, perchlorate and sulfate solutions at 25°C and one atmosphere total pressure in an oxygen free environment by increasing the pH with dilute sodium hydroxide. On aging the crystallinity of the precipitate increased and that was confirmed by X-ray diffraction patterns.

2.  $\text{Mn}_3\text{O}_4$ :

"Hausmannite" is the mineral name for this compound. Shomate (1943) obtained high purity  $\text{Mn}_3\text{O}_4$  by decomposition of electrolytic  $\text{MnO}_2$  at 1050°C. Millar (1928) prepared  $\text{Mn}_3\text{O}_4$  by thermal decomposition of manganous sulfate in air at 1000°C. Krull (1932) reduced  $\text{MnO}_2$  to  $\text{Mn}_3\text{O}_4$  with hydrogen

gas at 200°C.  $Mn_3O_4$  can be prepared from any of the oxides, hydrous oxides or hydroxides of manganese, as well as from a variety of manganese salts (e.g., chloride, nitrate and sulfate) merely by thermal decomposition in air at 1000°C.  $Mn_3O_4$  can also be prepared by oxidation of an aqueous suspension of manganous hydroxide (Feitknecht and Marti, 1945). Bricker (1965) prepared  $Mn_3O_4$  by oxidising  $Mn(OH)_2$  suspension (prepared by alkalisation of manganous nitrate, manganous sulfate and manganous chloride) with air purged of  $CO_2$  or with oxygen. Slow oxidation of  $Mn(OH)_2$  led to the formation of a cinnamon-brown compound which had an X-ray pattern identical to that of hausmannite. Electron micrographs showed that the product consisted of well formed crystals of pseudocubic habit. Chemical analysis of thus prepared  $Mn_3O_4$  yielded calculated formulas of  $MnO_{1.328}$ ,  $MnO_{1.338}$  and  $MnO_{1.338}$ . Morgan (1967) prepared hausmannite by air oxidation of  $2.3 \times 10^{-3}$  M  $Mn(ClO_4)_2$  in presence of 0.7 equivalents of NaOH per Mn(II) equivalent. The chemical analysis of the compound thus prepared yielded a calculated formula  $MnO_{1.31}$ .

### 3. $\gamma Mn_2O_3$ :

No natural occurrences of this compound have been described. It was found that upon prolonged oxidation in an aqueous environment cinnamon-brown  $Mn_3O_4$  became progressively darker in colour. Electron micrographs of this material showed crystals having a pseudocubic habit but generally less well developed and smaller in size than  $Mn_3O_4$ . X-ray patterns of samples taken periodically during the oxidation disclosed only the pattern of  $Mn_3O_4$ , but

chemical analysis yielded oxygen contents as high as  $\text{MnO}_{1.44}$ . Simon (1937) reported a preparation having the  $\text{Mn}_3\text{O}_4$  structure and the composition  $\text{MnO}_{1.48} 0.15\text{H}_2\text{O}$ . Moore et al. (1950) found that a compound could be prepared which had the structure of  $\text{Mn}_3\text{O}_4$  but very close to  $\text{MnOOH}$  in composition. Verwey and de Boer (1936) prepared a compound having the structure of  $\text{Mn}_3\text{O}_4$  but the composition  $\text{MnO}_{1.50}$ . They called this compound  $\gamma\text{Mn}_2\text{O}_3$ . Drotschmann (1960) prepared a compound having the hausmannite structure and the composition  $\text{MnO}_{1.39}$ . He found, on the basis of magnetic susceptibility measurements, that this compound should contain only the divalent and tetravalent states of manganese. Bricker (1965) prepared  $\gamma\text{Mn}_2\text{O}_3$  by strongly oxidising a suspension of  $\text{Mn}_3\text{O}_4$  with oxygen gas. Analysis of the material prepared yielded the formula  $\text{MnO}_{1.442 \pm 0.01} 0.49\text{H}_2\text{O}$ , close to  $\text{MnOOH}$ .  $\gamma\text{Mn}_2\text{O}_3$  was also prepared by air oxidation of  $2.3 \times 10^{-3}$  M  $\text{Mn}(\text{ClO}_4)_2$  in presence of 1.1 equivalents of  $\text{NaOH}$  per  $\text{Mn}(\text{II})$  equivalent the analysis of which yielded a formula  $\text{MnO}_{1.43}$ . (Morgan, 1967).

#### 4. Hydrohausmannite:

Feitknecht and Marti (1945) prepared a hydrous compound that had a manganese to oxygen ratio between  $\text{Mn}_3\text{O}_4$  and  $\text{MnOOH}$ , by oxidation of an aqueous suspension of  $\text{Mn}(\text{OH})_2$ . The X-ray diffraction pattern of this material was identical to that of hausmannite with the exception of a strong extra reflection in the low angle region and a general weakening of the intensities of the remaining reflections. It was believed that this compound was a hydrated form of



hausmannite, capable of some variation in manganese to oxygen ratio, and named it hydrohausmannite. Later on, Feitknecht et al. (1962) found that the material originally described by Feitknecht and Marti (1945) as hydrohausmannite was actually a mixture of two phases:  $\beta\text{MnOOH}$  and  $\text{Mn}_3\text{O}_4$ . Electron micrographs of their synthetic hydrohausmannite disclosed particles of two distinct morphologies: an equant morphology corresponding to  $\text{Mn}_3\text{O}_4$  and a platy hexagonal morphology corresponding to  $\beta\text{MnOOH}$ . A partial analysis of this material disclosed an oxygen to manganese ratio of 1.48. Bricker (1965) prepared a material having an X-ray pattern identical to natural hydrohausmannite from dilute  $\text{Mn}^{2+}$  solution ( $\approx 0.001\text{ m}$ ) by alkalisation with  $\text{NaOH}$  in presence of oxygen gas. Material precipitated from a highly oxygenated solution had a oxygen to manganese ratio of 1.50 indicating that the equant material in the mixture must be  $\gamma\text{Mn}_2\text{O}_3$  since  $\beta\text{MnOOH}$  has not been observed with an oxygen to manganese ratio exceeding 1.50. Materials precipitated from a less highly oxygenated solutions had oxygen to manganese ratios between 1.33 and 1.50.

##### 5. $\gamma\text{MnOOH}$ :

The mineral name for this compound is manganite. Feitknecht and Marti (1945) prepared  $\gamma\text{MnOOH}$  from manganous salt solutions by precipitation with ammonia in presence of hydrogen peroxide. Moore et al. (1950) prepared  $\gamma\text{MnOOH}$  by precipitation with ammonium hydroxide from manganous sulfate solution in the presence of hydrogen peroxide followed by drying at  $60^\circ\text{C}$  under vacuum. Bricker (1965)

prepared this compound by oxidising a suspension of  $\text{Mn}(\text{OH})_2$  with hydrogen peroxide. It was found that under prolonged oxidation with air or oxygen, a suspension of  $\text{Mn}(\text{OH})_2$  oxidised first to  $\text{Mn}_3\text{O}_4$ , then to  $\gamma\text{Mn}_2\text{O}_3$  and finally  $\gamma\text{MnOOH}$  began to form. If the initial oxidation was very rapid, some  $\beta\text{MnOOH}$  was also formed. Electron micrographs of  $\gamma\text{MnOOH}$  showed well formed crystals having a bladed habit. Complete conversion of  $\text{Mn}_3\text{O}_4$  to  $\gamma\text{MnOOH}$  with air or oxygen alone could not be accomplished over the duration of the experiments. Feitknecht et al. (1962) report that complete conversion of a mixture of  $\text{Mn}_3\text{O}_4$  and  $\beta\text{MnOOH}$  to  $\gamma\text{MnOOH}$  occurred after four months of oxidation with oxygen gas. Krishnan and Banerjee (1939) found that the magnetic anisotropy data for manganite indicated non-equivalent oxidation states for the manganese atoms. They suggested that half of the manganese atoms had an oxidation state of 2+ and the other half 4+, giving an overall average of 3+ for the compound. In an investigation of manganite using both X-ray and neutron diffraction methods, Dachs (1963) verified the earlier crystallographic work of Buerger (1936) giving refined atomic parameters, and showed that the hydrogen ions were bound to certain oxygens in the structure. On the basis of his study he concluded that the existence of mixed oxidation states (2+ and 4+) among the manganese atoms in this compound was highly improbable. Bricker (1965) favoured the conclusion of Dachs. An analysis of the compound indicated an oxidation grade of  $\text{MnO}_{1.51 \pm 0.01}$  (Bricker, 1965).

## 6. $\delta\text{MnO}_2$ :

The mineral name for this compound is birnessite.

McMurdie (1944) described an artificial manganese dioxide that gave an X-ray diffraction pattern consisting of two lines. He believed it to be a distinct species and proposed a name  $\delta\text{MnO}_2$  for this compound. Feitknecht and Marti (1945) prepared compounds varying in composition between  $\text{MnO}_{1.74}$  and  $\text{MnO}_{1.82}$  by oxidation of ammonical aqueous suspensions of manganous hydroxide with hydrogen peroxide, and between  $\text{MnO}_{1.82}$  and  $\text{MnO}_{1.96}$  by reduction of  $\text{KMnO}_4$  solutions with HCl or hydrogen peroxide. These compounds all gave similar X-ray patterns; however, some contained more reflections than others. They called these compounds manganous manganites and considered them to be double-layer compounds with varying degrees of order. They suggested that these compounds could be represented by a formula  $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . Cole et al. (1947) and Copeland et al. (1947) found that air oxidation of alkaline manganous solutions yielded a product with an X-ray pattern identical to manganous manganite. The compounds prepared by Copeland et al. (1947) varied in oxidation grade between  $\text{MnO}_{1.80}$  and  $\text{MnO}_{1.96}$ . Burser et al. (1954) investigated the substances described as  $\delta\text{MnO}_2$  and manganous manganite. Although it was concluded that manganous manganite and  $\delta\text{MnO}_2$  were the same phase, they recommended retaining both names based on X-ray diffraction patterns,  $\delta\text{MnO}_2$  to describe compounds with an oxidation grade above  $\text{MnO}_{1.90}$ , and manganous manganite to describe those with an oxidation grade below  $\text{MnO}_{1.90}$ .

Glemser et al. (1961) discussed the preparation and properties of  $\delta\text{MnO}_2$ . They found that  $\delta\text{MnO}_2$  with an oxidation grade upto 1.99 could be prepared, and divided the preparations into three subtypes ( $\delta$ ,  $\delta'$ ,  $\delta''$ ) on the basis of the intensity and sharpness of X-ray reflections. Bricker (1965) concluded that presence or absence of basal reflections was a function of particle size rather than oxidation grade. Differences in the particle size of this compound were related to preparation procedures. On this basis he suggested that the name manganous manganite be dropped and these compounds be referred to as  $\delta\text{MnO}_2$ . Electron micrographs of  $\delta\text{MnO}_2$  showed material of platy appearance with very poorly developed crystal faces. Morgan (1967) prepared this compound by air oxidation of  $2.3 \times 10^{-3}$  M  $\text{Mn}(\text{ClO}_4)_2$  in presence of 18 equivalents of NaOH per Mn(II) equivalent. The chemical analysis of the compound thus prepared yielded a calculated formula  $\text{MnO}_{1.90}$ .

#### 7. $\gamma\text{MnO}_2$ :

"Nsutite" is the mineral name for this compound. Glemser (1939) prepared an oxide by three different methods: oxidation of a boiling  $\text{MnSO}_4$  solution containing  $\text{KNO}_3$  with ammonium persulfate, oxidation of a boiling  $\text{MnSO}_4$  solution containing  $\text{KNO}_3$  with potassium permanganate, and decomposition of permanganic acid at  $45^\circ\text{C}$ . The oxidation grades of this oxide prepared by three different methods were found to be  $\text{MnO}_{1.76}$ ,  $\text{MnO}_{1.84}$  and  $\text{MnO}_{1.93}$ . Boiling these compounds in nitric acid increased the ratio to  $\text{MnO}_{1.97}$  in each case. Glemser proposed a name  $\gamma\text{MnO}_2$  for this compound.

Bricker (1965) prepared  $\gamma\text{MnO}_2$  by acidifying  $\text{Mn}_3\text{O}_4$  suspension. He also observed that mild acidification of  $\text{Mn}_3\text{O}_4$  produced  $\delta\text{MnO}_2$  whereas, intense acidification produced  $\gamma\text{MnO}_2$ . Electron micrographs  $\gamma\text{MnO}_2$  showed well developed acicular crystals.

## 2.8 The Use of Oxides of Manganese as Sorbents

Among the various compounds of manganese only  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  have been used as sorbents by many researchers. Oxidation of  $\text{Mn}^{2+}$  ions occurring in natural waters or the reduction of  $\text{KMnO}_4$  (used in certain treatment processes), leads to the formation of colloidal  $\delta\text{MnO}_2$ . The high surface area, as high as  $300 \text{ m}^2/\text{g}$ , of the colloidal  $\delta\text{MnO}_2$  exerts dominating influence on the concentration and distribution of many elements in the aquatic environment, e.g., the concentration of heavy metals in the sea. Reported  $\text{pH}_{\text{zpc}}$  values for the hydrated  $\delta\text{MnO}_2$  lie between 2 and 3.8. Hence, in the pH range of natural waters,  $\delta\text{MnO}_2$  exhibits a net negative charge, and the strong dependence of the adsorption of cations on pH, can be understood on the basis of pH dependent surface charge (Gray, 1981). The high adsorption capacity of  $\delta\text{MnO}_2$  may be ascribed to high proportion of available vacancies on the exterior surfaces on each side and within the sheets of the  $[\text{MnO}_6]$  octahedra making up the crystal structure (Burns, 1976).

Touhill (1964) demonstrated the feasibility of using  $\delta\text{MnO}_2$  to remove  $^{137}\text{Cs}$ ,  $^{131}\text{Ce}$ , and  $^{90}\text{Sr}$  from aqueous solution. Posselt and Weber (1974) studied the sorption of cadmium on hydrous oxides of aluminium, iron and manganese. He observed

that the sorption capacity of manganese dioxide ( $\delta\text{MnO}_2$ ) was greater than that of iron and aluminium oxides. He suggested the use of hydrous  $\text{MnO}_2$  as a suitable treatment for the removal of cadmium in water and wastewater. Loganathan and Bureau (1973) demonstrated the ability of  $\delta\text{MnO}_2$  to sorb  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . Morgan and Stumm (1964) observed high capacity of  $\delta\text{MnO}_2$  to adsorb  $\text{Mn}^{2+}$  ions. Gadde and Laitinen (1974) used  $\delta\text{MnO}_2$  to adsorb  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ti}^{2+}$ . Colthurst and Singer (1982) studied the removal of trihalomethane (THM) precursors by permanganate oxidation and  $\delta\text{MnO}_2$  sorption. Gabano et al. (1965) studied the removal of various metal ions by sorption on  $\gamma\text{MnO}_2$ . McKenzie (1970) studied the sorption of Co and other heavy metal ions by several manganese oxides.

Instead of using the oxide as a sorbent, a few workers impregnated various materials with manganese oxides and studied the sorption capacity of impregnated materials. Moore and Reid (1973) impregnated acrylic fibres with manganese dioxide and removed radium from a contaminated well water successfully. Similar work regarding sea water and brackish water containing high levels of calcium and magnesium was also reported to be successful and a figure of 96% removal of radium by adsorption has been reported (Kosarek, 1979). Cerling and Turner (1982) reported that iron and manganese oxide coatings on gravel in stream beds adsorbed  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$  and  $^{137}\text{Ce}$  rapidly from water. Karthikeyan (1982) and Jayasimha (1983) used Giridih bituminous

coal impregnated with manganese oxide for the removal of mercury and THM precursors from water, respectively.

Hudson et al. (1974) impregnated ground corncob and saw dust with  $\delta\text{MnO}_2$  and observed that the performance of the impregnated sorbents was many times greater than that of activated carbon.

### 3. SCOPE OF THE PRESENT STUDY

Among the treatment processes available for removal of mercury, adsorption seems to be capable of reducing the mercury concentration below 0.001 mg/l, the prescribed limit for safe drinking water supplies. Adsorption on activated carbon is very effective and competitive in the removal of mercury at trace quantities. But, producing a good quality of activated carbon is often beyond the reach of the developing countries. In addition, cost of production and effective regeneration of activated carbon is very high. At this stage it is highly desirable to find an alternate to activated carbon. From a review of the literature it is evident that a few workers were successful in developing low cost sorbents through chemical pretreatment of coal, coconut shell, etc. Besides activated carbon,  $\delta\text{MnO}_2$  proved its ability to adsorb heavy metals and organics. For this reason  $\delta\text{MnO}_2$  was used by a few investigators to impregnate acrylic fibres, saw dust, ground corn cob, etc. in an attempt to develop low cost sorbents. However, except the limited study by Karthikeyan (1982) there has been no investigation on enhancement of mercury sorption capacity of coal through manganese impregnation. The present study was undertaken to investigate in greater details sorption of mercury by coal through impregnation of the various oxides of manganese. The study was undertaken along the following lines:



1. Impregnating Giridih bituminous coal with four different oxides of manganese, viz.,  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$ ,  $\gamma\text{MnOOH}$  and  $\gamma\text{Mn}_2\text{O}_3$ .
2. Characterising the sorbents developed.
3. Evaluating the effect of the impregnation in terms of mercury sorption through batch sorption tests against untreated Giridih bituminous coal and a standard activated carbon (Filtrisorb-400).
4. Studying the reusability of sorbents through regeneration studies.

#### 4. MATERIALS AND METHODS

##### 4.1 Glassware

All glassware used in the present study was of 'Pyrex' quality manufactured by Borosil Glass Works Ltd., Bombay and marketed under the brand name 'Corning'. The glassware was soaked overnight in a 10 mg/l of mercury solution to minimise the possibility of mercury sorption by glass as suggested by Masri and Friedman (1973). The excess mercury was washed off with nitric acid and glass-distilled water prior to use. It was expected that this procedure would effectively saturate the active sites on the glass so that additional mercury would not be sorbed. After a sorption experiment all glassware was washed with tapwater and with distilled water and kept ready for further use.

##### 4.2 Water

Water used in all experiments was laboratory distilled water redistilled using a glass distillation still. The pH of this water was in the range 6.7-6.9 and the specific conductivity varied between 4.2 and 6.4 microsiemens/cm.

##### 4.3 Chemicals

All chemicals used were of analytical reagent grade. Stock mercury solution was prepared and this was used to prepare working solutions for daily experimental work (Standard Methods for the Examination of Water and Wastewater, 1976).

#### 4.4 Sorbents and Preparation

Giridih bituminous coal (GBC) obtained through Water Treatment Division, NEERI, Nagpur was used in the present study. The proximate and ultimate analyses and physical properties of Giridih bituminous coal are given in Tables 4 and 5. To evaluate the effect of impregnation of oxides of manganese on GBC in terms of mercury sorption, untreated GBC and a standard activated carbon (Filtrisorb-400, manufactured by Calgon Corporation, Pittsburgh, Pa., U.S.A.) were used as references. GBC was used because of its high equilibrium sorption which is comparable to that of activated carbons (Pandey and Chaudhuri, 1982). Four oxides of manganese, viz.,  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$ ,  $\gamma\text{MnOOH}$  and  $\gamma\text{Mn}_2\text{O}_3$  were chosen with a view to investigate the effect of impregnation of oxides of manganese over a wide oxidation grade.  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}(\text{OH})_2$  were not chosen because of their instability.

The activated carbon and coal samples were ground and sieved to a geometric mean size of  $388\mu\text{m}$  ( $355\text{--}425\mu\text{m}$ ), washed with distilled water to remove the fines and adhered impurities and dried at  $103^\circ\text{C}$  for use in sorption experiments. Karthikeyan (1982) and Jayasimha (1983) used coal of a geometric mean size  $63.05\mu\text{m}$  to impregnate oxides of manganese. The methods used in their studies for separating the impregnated coal and the excess oxide are questionable in view of the homogeneity of the sorbents. Hence, in the present study coal of a geometric mean size  $388\mu\text{m}$  was chosen to facilitate the separation of excess oxide and impregnated coal. The ratio between manganese contributing

Table 4

Proximate and Ultimate Analyses of Giridih Bituminous Coal  
(Pandey and Chaudhuri, 1982)

Specification	Proximate analysis	Ultimate analysis
Moisture* %	4.60	4.60
Ash %	18.80	20.68
Volatile %	31.60	
Fixed carbon %	45.00	
Carbon %		61.62
Hydrogen %		3.38
Sulfur %		0.33
Nitrogen %		1.31
Oxygen % (by difference)		8.08

\* At 60% R.H., 40°C.

Table 5

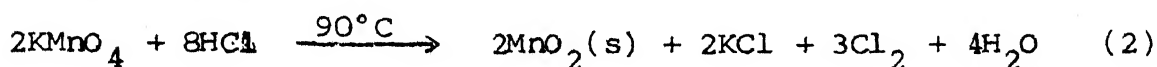
Physical Properties of Giridih Bituminous Coal  
(Paramasivam and Deshpandey, 1972)

Specific gravity	1.33
Moh's hardness	2-3
Durability test (% loss in weight after 100 h of back washing)	0.63
Solubility in dilute hydrochloric acid (10% V/V)	0.69%
Sphericity	0.74-0.76
Phenol leaching	Not detectable

to the formation of oxide and coal was kept 0.372 in the impregnation of the oxides on coal, in order to facilitate a comparison of the efficiencies of the impregnated sorbents. This ratio was decided based on the impregnation works carried out by previous researchers. Procedures for impregnating the four oxides are outlined below.

1. Procedure for Impregnating  $\delta\text{MnO}_2$ :

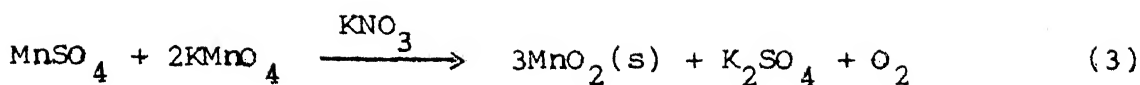
$\delta\text{MnO}_2$  was prepared by the following reaction, but with an excess  $\text{KMnO}_4$  to ensure oxidising conditions (Burser *et al.*, 1954).



325 ml of 0.5 M  $\text{KMnO}_4$  and 300 ml of 2 M  $\text{HCl}$  were taken in two separate beakers and warmed to  $90^\circ\text{C}$  in a steam bath. 24 g of coal was added to  $\text{KMnO}_4$  and stirred for 10 min keeping the temperature of the mixture at  $90^\circ\text{C}$ . To this,  $\text{HCl}$  was added slowly with constant stirring for one min. Stirring was continued for 10 more min. The supernatant containing only excess precipitate was carefully decanted. The oxide loosely adhered to the coal was washed off several times with redistilled water and then a few times with 0.05 M  $\text{HClO}_4$  to remove as much potassium as possible. The impregnated coal was dried for 24 h at  $45^\circ\text{C}$ , the temperature specified for drying  $\delta\text{MnO}_2$ .

2. Procedure for Impregnating  $\gamma\text{MnO}_2$ :

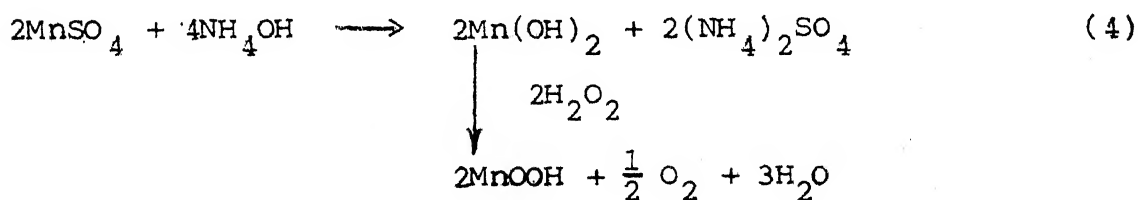
$\gamma\text{MnO}_2$  was prepared as suggested by Glemser (1939). The formation of  $\gamma\text{MnO}_2$  may be described by the following reaction.



100 g of coal was added to 225 ml of boiling 1 M  $\text{MnSO}_4$  solution containing 2 g of  $\text{KNO}_3$  (a catalyst for the reaction between  $\text{MnSO}_4$  and  $\text{KMnO}_4$ ). The mixture was stirred for 10 min. This was oxidised by the addition of 450 ml of 1 M  $\text{KMnO}_4$ . The stirring was continued for 10 more min, allowing the mixture to boil. The supernatant containing the excess precipitate was carefully decanted. The oxide loosely adhered to the coal was washed off several times with redistilled water till a clear supernatant was obtained. The impregnated coal was dried for 24 h at  $45^\circ\text{C}$ , the temperature specified for drying  $\gamma\text{MnO}_2$ .

### 3. Procedure for Impregnating $\gamma\text{MnOOH}$ :

$\gamma\text{MnOOH}$  was prepared as suggested by Moore et al. (1950). The formation of  $\gamma\text{MnOOH}$  may be described by the following reaction.



50 g of coal was added to 1350 ml of 0.25 M  $\text{MnSO}_4$  and stirred for 10 min. This was oxidised by adding 41 ml of 30 percent (W/V)  $\text{H}_2\text{O}_2$ . The sulfate and peroxide were mixed and 400 ml of 2 M  $\text{NH}_4\text{OH}$  was added to this. After the addition of the base the mixture was boiled in a water bath for 10 min with constant stirring. The supernatant containing only excess precipitate was carefully decanted. The oxide

loosely adhered to the coal was washed off several times with redistilled water till a clear supernatant was obtained. The impregnated coal was dried at 60°C under vacuum (10 mm of Hg) for 72 h, the conditions specified for drying  $\gamma\text{MnOOH}$ .

#### 4. Procedure for Impregnating $\gamma\text{Mn}_2\text{O}_3$ :

According to Morgan (1967) the extent of oxygen uptake during air oxidation of solutions of Mn(II) salts in presence of a base is a function of quantity of base added. If the quantity of strong base added is insufficient to precipitate all or nearly all the Mn(II) present in an oxygenating system, the oxygen uptake in the system depends upon the relative deficiency of the base. He found that  $\gamma\text{Mn}_2\text{O}_3$  ( $\text{MnO}_{1.43}$ ) can be prepared by air oxidation of Mn(II) solution in presence of 1.1 equivalents of NaOH per Mn(II) equivalent. In the present study this method was used to prepare  $\gamma\text{Mn}_2\text{O}_3$ .

50 g of coal was added to 1000 ml of 0.34 M  $\text{MnSO}_4$  solution and the mixture was stirred for 10 min. To this 1000 ml of 1.025 M NaOH was added and the stirring was continued for 10 more min. Then the sample was aerated for 12 h with compressed air. Formation of black precipitate was observed. The supernatant containing only excess precipitate was carefully decanted. The oxide loosely adhered to the coal was washed off several times with redistilled water till a clear supernatant was obtained. The impregnated coal was dried for 24 h at 45°C, the temperature specified for drying  $\gamma\text{Mn}_2\text{O}_3$ .

## 4.5 Sorbent Characterisation

### 4.5.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is an instrument similar in purpose to the ordinary light microscope, but with a much greater resolving power.\* The resolving power of a scanning electron microscope is of the range  $0.2\text{ }\mu\text{m}$ – $0.5\text{ }\mu\text{m}$  when compared with that of an optical microscope whose range is  $5\text{ }\mu\text{m}$ – $0.1\text{ }\mu\text{m}$  (Hearle et al., 1973). Instead of a beam of light to illuminate the object, a parallel beam of electrons from an electron gun\*\* is used. In SEM a thick sample can be used and the sample is scanned by the electron beam. Secondary electrons emitted from the surface of the sample are focussed into a screen. The magnification is less for SEM compared to transmission electron microscope, but a three-dimensional image is obtained.

Scanning electron microscope was used to study the surface characteristics of a polymer carbon and Amberlite IRA-938 ion exchange resin (Neely and Isacoff, 1982) and stainless steel coated with  $\text{TiO}_2$  (Hasselberger et al., 1974). In the present study, scanning electron micrographs were taken on an ISI-60 (International Scientific Instruments-60) scanning electron microscope in the secondary electron

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\* Resolving power is the ability of an optical system (e.g. microscope, telescope, eye, etc.) to produce separate images of objects very close together.

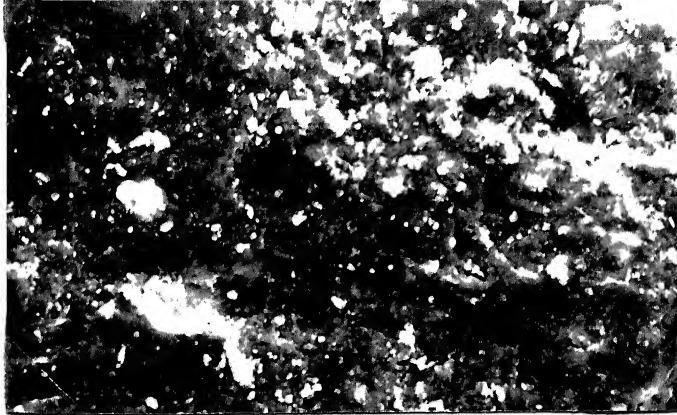
\*\* Electron gun is a source of electrons in a cathode ray tube or electron microscope. It consists of a cathode emitter of electrons, an anode with an aperture through which the beam of electrons can pass, and one or more focussing and control electrodes.



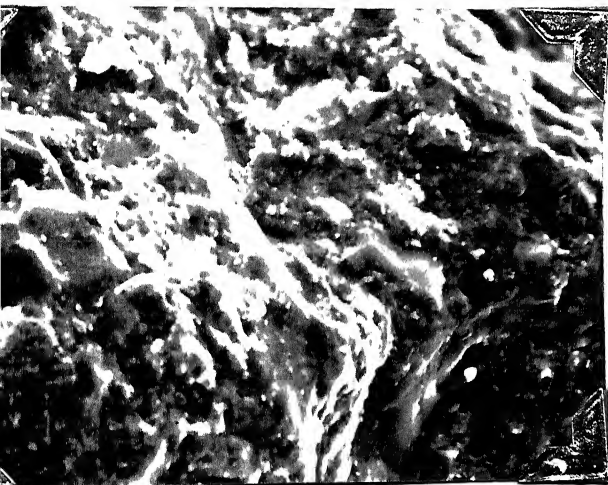
mode of operation. The scanning electron micrographs were taken to confirm the oxide impregnation on coal and to study the surface characteristics of the impregnated coal sorbents. The micrographs presented on pages 46 and 47 are of two different magnifications, viz., 250X and 1000X, for each sorbent. Two magnifications were chosen for a better appreciation of the technique in analysing the micrographs. The following statements can be made based on careful observation of the micrographs.

1. The definite change in the microstructure, for example, from discrete particles to band like structure, between the untreated coal and treated coals is associated with the impregnation of the oxides of manganese.
2. The tendency for the band like structure seems to increase with increase in oxidation grade.
3. There is a definite difference between coal sorbents impregnated with  $\delta\text{MnO}_2$ , and  $\gamma\text{MnO}_2$  and coal sorbents impregnated with  $\gamma\text{MnOOH}$ , and  $\gamma\text{Mn}_2\text{O}_3$ . This may be correlated with the significant difference in the oxidation grades of manganese in the two cases.
4. It is difficult to draw conclusions about pore size distribution and pore volume from the limited number of micrographs.

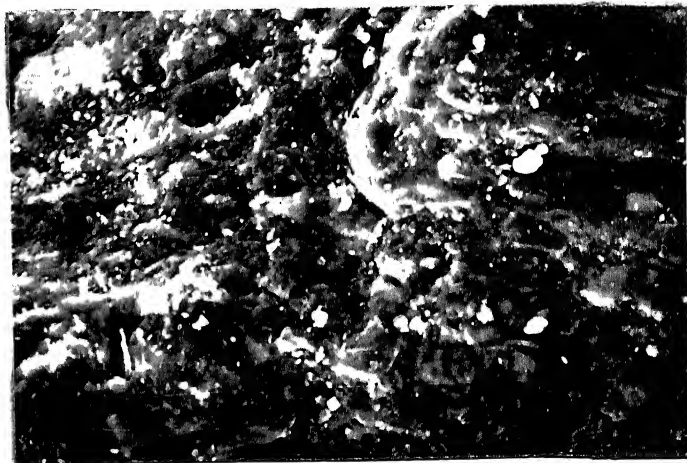
In the micrographs the white regions represent the portion wherefrom the number of secondary electrons emitted is large and the dark regions represent the portion wherefrom the number of secondary electrons emitted is small. The number of secondary electrons emitted from a particular



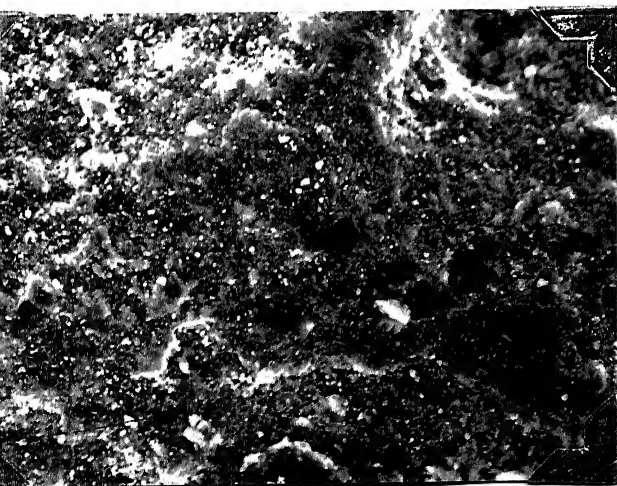
GBC



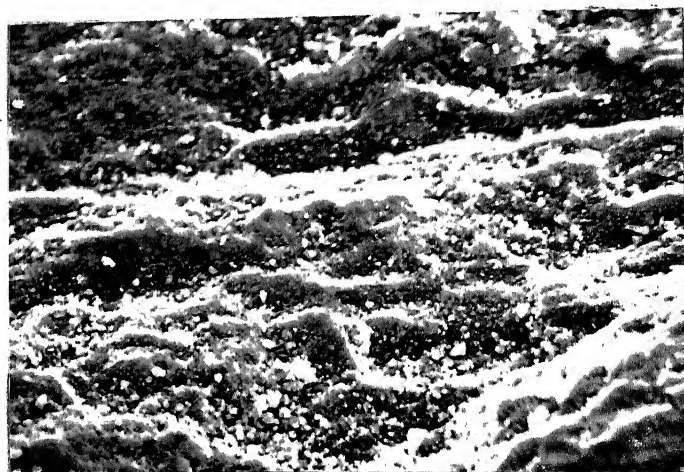
GBC +  $\gamma\text{Mn}_2\text{O}_3$



GBC +  $\gamma\text{MnOOH}$

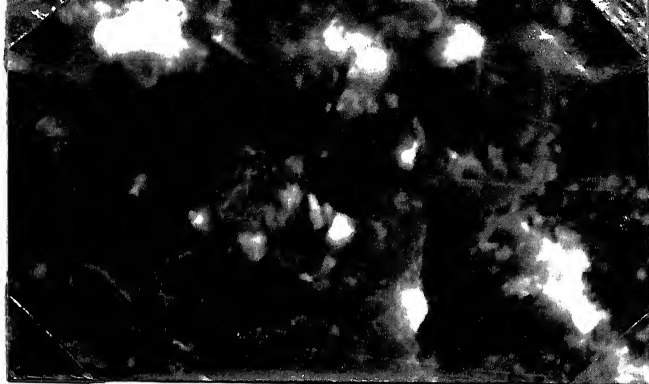


GBC +  $\gamma\text{MnO}_2$

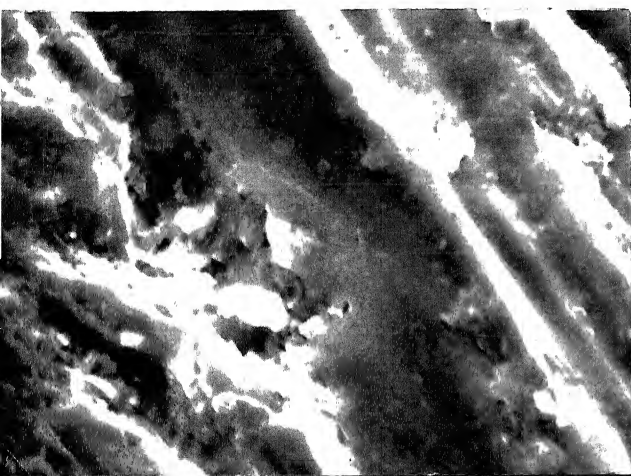


GBC +  $\delta\text{MnO}_2$

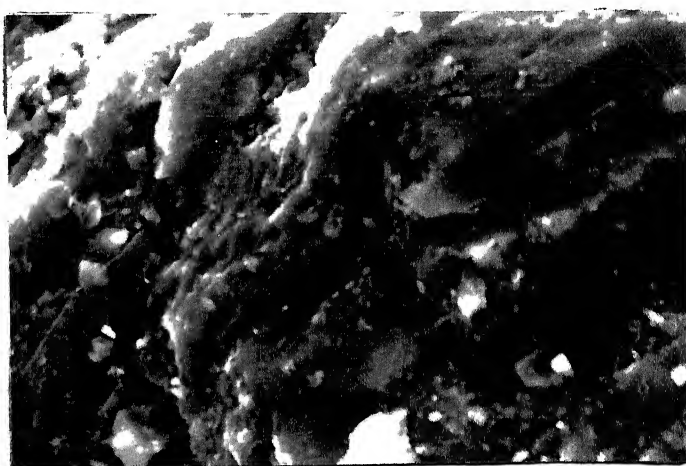
Scanning Electron Micrographs of GBC and GBC Impregnate  
with Oxides of Manganese (Magnification: 250X).



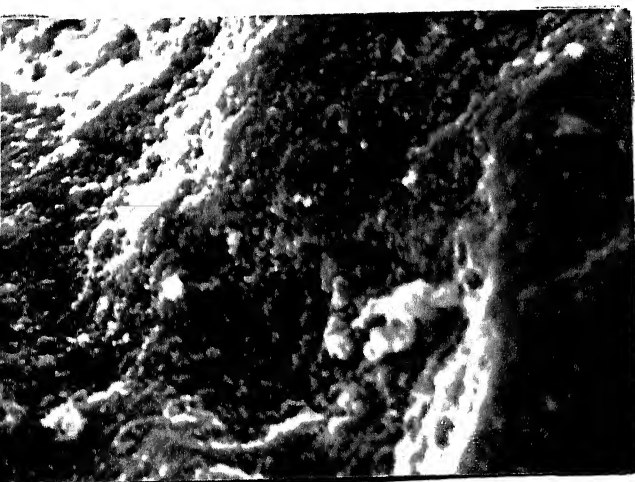
GBC



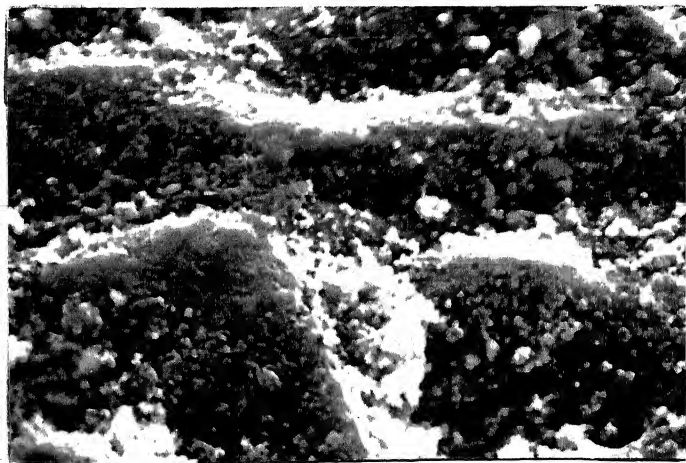
GBC +  $\gamma\text{Mn}_2\text{O}_3$



GBC +  $\gamma\text{MnOOH}$



GBC +  $\gamma\text{MnO}_2$



GBC +  $\delta\text{MnO}_2$

Scanning Electron Micrographs of GBC and GBC Impregnated with Oxides of Manganese (Magnification: 1000X).

phase depends upon topography and composition of the phase, and angle of incidence of the electron beam.

#### 4.5.2 Iodometry

The iodometric test remains to be the most precise and reliable titrimetric procedure for dissolved oxygen (DO) analysis of water and wastewater in environmental engineering practice. The test is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass-stoppered bottle. DO present in the sample rapidly oxidises  $Mn^{2+}$  to a higher state of valence under the alkaline conditions. In presence of iodide ions and acidification, the oxidised manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content in the sample. The iodine is then titrated with a standard solution of thio-sulfate. This principle has been used in the present study to estimate the oxidation grade of manganese in the oxides of manganese under consideration. The oxides of manganese were prepared using procedures outlined in Section 4.4 but excluding only coal during the precipitation. The following steps illustrate the procedure followed.

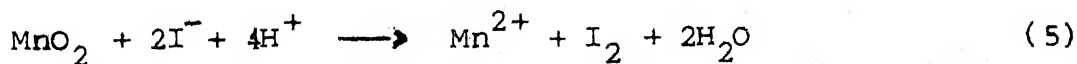
1. About 240 ml of glass-distilled water was taken in a 500 ml conical flask. To this 2 g KI (amount of KI required was determined by conducting experiments, taking varying amounts of KI to oxidise a known amount of oxide of manganese. Slightly more than the required amount was taken to accelerate the reaction between  $I^-$  ions and the oxidant as suggested by Alexeyev (1979))

and 2 ml  $\text{H}_2\text{SO}_4$  were added. If there was any brown or yellow colour formation indicating the liberation of iodine due to the impurity  $\text{KIO}_3$  in  $\text{KI}$ , the solution was titrated very carefully with 0.025 N standard sodium thiosulfate till the colour disappeared to eliminate the error in the estimation. If the colour was not formed it was not titrated with thiosulphate.

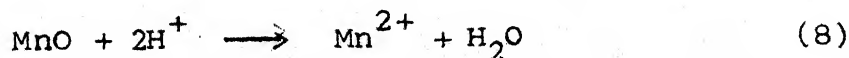
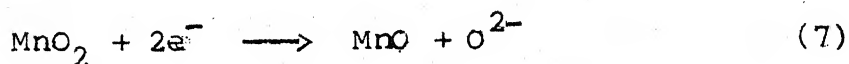
2. 0.05 g of the oxide of manganese was added to this and made upto 250 ml by adding glass-distilled water. The reaction mixture was kept in dark for 10 min for liberation of iodine.
3. A 50 ml aliquot of the reaction mixture was titrated with 0.025 N sodium thiosulfate solution to a pale straw colour. Then a drop of starch solution was added and it was further titrated till the blue colour formed after the addition of starch was completely discharged. The volume of the titrant was recorded ( $V_1$ ). This was repeated twice and the average value was recorded as 'V'.

Calculation:

The reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  is represented by the following mechanism.



Equation (5) may be explained by the following steps





From equations (6) and (7) it can be said that one mole of iodine liberated is equivalent to 0.5 moles of oxygen. That is, if one mole of  $\text{MnO}_2$  is reduced to  $\text{Mn}^{2+}$ ,  $\text{I}_2$  equivalent to only 16 g of oxygen will be liberated. Since

$$\begin{aligned} 1.0 \text{ ml of } 0.025 \text{ N sodium thiosulfate} &= 200 \mu\text{g DO} \\ V \text{ ml of } 0.025 \text{ N sodium thiosulfate} &= 200 V \mu\text{g DO} \\ &= Y \text{ mg} \end{aligned}$$

If the oxide under consideration were to be  $\text{MnO}_2$ , 0.05 g of that will give rise to 9.20 mg of oxygen.

If the oxide under consideration has an oxidation grade  $\text{MnO}_x$ ,

$$x = \frac{Y(10)}{9.20}$$

The oxidation grades of manganese thus calculated, are shown in Table 6. The values obtained are comparable with the values reported in the literature.

Table 6  
Oxidation Grades of Oxides of Manganese

Oxide of manganese	Oxidation grade
$\delta\text{MnO}_2$	$\text{MnO}_{1.89}$
$\gamma\text{MnO}_2$	$\text{MnO}_{1.83}$
$\gamma\text{MnOOH}$	$\text{MnO}_{1.50}$
$\gamma\text{Mn}_2\text{O}_3$	$\text{MnO}_{1.42}$

#### 4.5.3 Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA is otherwise known as XPS (X-ray photoelectron spectroscopy or X-ray photoemission spectroscopy). Among the electron spectroscopies photoemission plays a special role; it combines both optical and spectroscopic methods. Stimulation of the sample under observation occurs by absorption of photons, and the electrons emitted as a response are observed. In XPS the resolution limit is given by the width of the characteristic X-ray line used to photoemit the electrons. Photon energies in the range 0.1-5 KeV are sufficient to excite core electrons, giving sharp characteristic lines in the spectra. The accurate observation of core levels makes this type of spectroscopic element specific providing a powerful tool for chemical analysis. Valence states may be directly observed by this instrument. Usually the resolution is not sufficient to show fine details, unless an X-ray monochromator is used to reduce the line width of the light source which is normally of the order of 1-3 mm (Ibach, 1977).

In the present study, this technique was used to estimate the oxidation grade of manganese present on the surface of impregnated coal. This was done to know whether the oxide of manganese had undergone any change after impregnation on coal. XPS (Model-550 manufactured by Perkin Elemer, U.S.A.) was used in Mg-K $\alpha$  mode of operation (photon energy 1.2 KeV). An attempt was made to estimate

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the oxidation grade of manganese on coal along the following lines.

1. Determining the binding energy of manganese present in various oxidation grades using XPS.
2. Plotting a graph between shift in binding energy  $\Delta E$  and the oxidation grade of manganese, where  $\Delta E = E_{Mn^{x+}} - E_{Mn^0}$ .  
 $E_{Mn^{x+}}$  = the binding energy of manganese whose oxidation state is  $x+$  and  $E_{Mn^0}$  = the binding energy of elemental manganese.
3. Determining the binding energy of manganese present on coal (the impregnated coal was sealed at high vacuum ( $10^{-6}$  torrs) created by employing rotary pump and mercury diffusion pump in series. A liquid- $N_2$  trap also was employed to condense the vapours, viz., water vapour, oil vapour,  $CH_4$ , etc., that may come out from impregnated coal under high vacuum. This was done as a preventive measure for the possible damage to the instrument, which operates under ultrahigh vacuum, due to the liberation of the vapours during the analysis).
4. Estimating the oxidation grade of manganese present on coal knowing its binding energy, from the calibration curve.

The XPS did not detect presence of manganese on the impregnated coal. From this, it could be said that manganese was not present in concentrations greater than 1 percent in the outer 30 Å layer of the sample. Conclusions could not be drawn about the presence of manganese in bulk material (excluding 30 Å outerlayer of the sample) since



the instrument was sensitive only to a depth of 30 Å and concentrations greater than 1 percent.

#### 4.5.4 Pore Size Distribution and Surface Area

Pore size distribution, pore volume and surface area of the sorbents used in this study were obtained through Projects and Development India Ltd., Sindri. Nitrogen-BET adsorption and mercury porosimetry were employed for analysis. The values are given in Table 7.

The results show a marked increase in the pore volume of all impregnated sorbents against untreated coal. Increase in surface area could be detected only in the case of  $\text{MnO}_2$  impregnated coal. The surface area value of Filtrasorb-400 is in agreement with the value reported by Huang & Ostavic(1978).

#### 4.5.5 $\text{pH}_{\text{zpc}}$

The pH of zero point charge ( $\text{pH}_{\text{zpc}}$ ) of all the impregnated coals were determined by fast alkalimetric titration method (Huang and Ostavic, 1978). To four identical portions of 100 ml solution containing known amount of NaCl ( $10^{-1}$  M,  $10^{-2}$  M and  $10^{-3}$  M), 1 g of sorbent was added. The samples were agitated for 20 h at 20 rpm. Out of the two samples (with sorbent), one was titrated with acid (0.1 N HCl) and the other with base (0.1 N NaOH). The pH values were recorded after the addition of each aliquot of the titrant. The other two samples were allowed to settle for separating the sorbent. The supernatants were titrated as before. The net titration curve for each ionic strength was obtained by subtracting the titration curve of the supernatant from that of the sample (with sorbent). In

Surface Area, Pore Volume and Pore Size Distribution

Sorbent	Surface area m <sup>2</sup> /g	Pore volume cc/g	Pore size distribution (% by volume)						
			4-60 nm	60-100 nm	100-200 nm	200-300 nm	300-400 nm	400-500 nm	500-750 nm
GBC	1	0.0296	0	0	16.7	15.5	7.1	8.3	52.4
GBC + δMnO <sub>2</sub>	13.3	0.0507	31.7	10.6	12.2	9.7	4.1	1.6	30.1
GBC + γMnO <sub>2</sub>	1	0.0451	34.7	9.3	10.3	5.7	4.7	3.1	32.2
GBC + γMnOOH	1	0.0592	13.3	6.2	6.7	3.3	0.8	2.5	67.2
GBC + γMn <sub>2</sub> O <sub>3</sub>	1	0.0706	66.8	6.0	5.7	2.8	1.6	0.8	16.3
Filtrisorb-400	946.1	0.7894	64.2	3.9	4.1	2.4	1.4	1.0	23.0

absence of specific chemical interaction between the single electrolyte and the surface, the net titration curves usually meet at a point that is defined as the  $\text{pH}_{\text{zpc}}$  (Huang, 1977).

The net titration curves for coal impregnated with  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$ ,  $\gamma\text{MnOOH}$ , and  $\gamma\text{Mn}_2\text{O}_3$  were prepared to obtain pH of zero point charge. A typical set of net titration curves is shown in Figure 3. The values of  $\text{pH}_{\text{zpc}}$  of the impregnated sorbents used in the present study are given in Table 8. The table also includes Giridih bituminous coal and Filtrasorb-400 for which the values reported by Karthikeyan (1982) are used.

Table 8  
 $\text{pH}_{\text{zpc}}$  of Sorbents Used in the Present Study

Sorbent	$\text{pH}_{\text{zpc}}$
Giridih bituminous coal	7.0-7.15
Filtrasorb-400	6.75
GBC impregnated with $\delta\text{MnO}_2$	4.50
GBC impregnated with $\gamma\text{MnO}_2$	5.75
GBC impregnated with $\gamma\text{MnOOH}$	6.75
GBC impregnated with $\gamma\text{Mn}_2\text{O}_3$	8.00

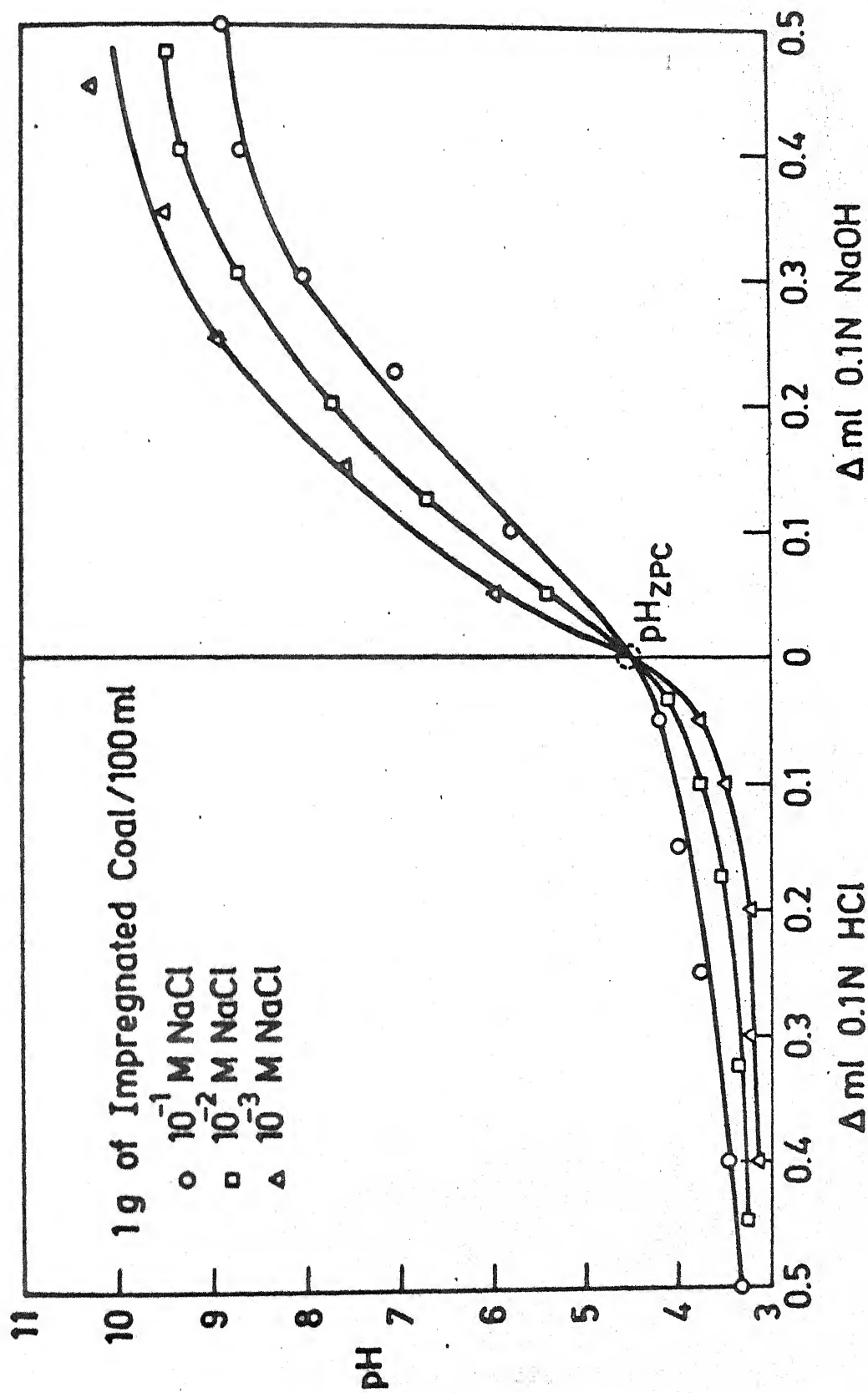


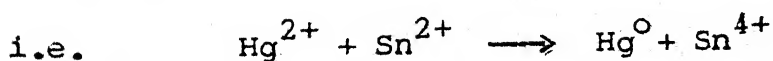
Fig. 3. Net Titration Curves for Giridih Bituminous Coal Impregnated with  $\delta$ -MnO<sub>2</sub> in Presence of Various Concentrations of NaCl.

#### 4.6 Estimation of Mercury

Mercury concentration was estimated using a mercury analyser (MA 5800A, manufactured by Electronics Corporation of India Limited, Hyderabad, India) with the following specifications.

Measuring range in solutions:	20-200 ng absolute
Sensitivity	: 3 ng absolute for 1 percent absorption
Short term fluctuations	: +1 percent of full scale deflection
Vapour generating system	: All glass reaction assembly (one set) with magnetic stirrer and wooden stand
Read-out	: 125 mm dial read-out graduated in optical density/transmittance
Radiation source	: Mercury lamp
Wavelength	: 253.7 nm
Detector	: IP 28 photomultiplier
Input power requirements	: 230 V, 50 Hz, 40 VA
Dimensions (main unit)	: 400 mm x 300 mm x 230 mm.

The MA5800A is a cold vapour atomic absorption spectrophotometer based on the principle that mercury vapour (atoms) absorbs resonance radiation at 253.7 nm. The method depends on the reduction of available mercury in a reducible state (mainly  $\text{Hg}^{2+}$ ) to the elemental state by reaction with stannous chloride.



The carrier gas (air free from mercury) bubbles through the vapour generation system, carries elemental mercury from

the solution and then passes through the absorption cell which is irradiated by a low pressure mercury vapour lamp. Mercury vapour absorbs the radiation at 253.7 nm and causes a change in the transmittance/absorbance, which can be correlated to the total mercury content in the sample solution.

The instrument is initially calibrated for known concentrations and then the unknown concentration in the sample is determined. The calibration curve for 12 ml total volume is shown in Figure 4.

#### 4.7 Experimental Techniques

##### 4.7.1 Batch Sorption Tests

Batch sorption experiments were conducted at room temperature (32-34°C) in a rotary shaker @ 40 rpm to take care of bulk diffusional resistance (Pandey, 1978). The reaction bottles were turned end-over-end in the shaker. The reaction mixture consisted of a total volume of 200 ml containing 500 mg/l of the sorbent and the desired concentration of mercury.

For kinetic studies, an initial mercury concentration of 100 µg/l was used keeping in view of the real-world concentrations, e.g., the effluent of a treatment plant where sulfide precipitation is practised for removal of mercury. Number of reaction bottles were employed for each test depending upon the requirement. The bottles were withdrawn at the end of the desired contact time and the samples were analysed for mercury. Temperature and pH of the reaction mixture were recorded initially and at the end

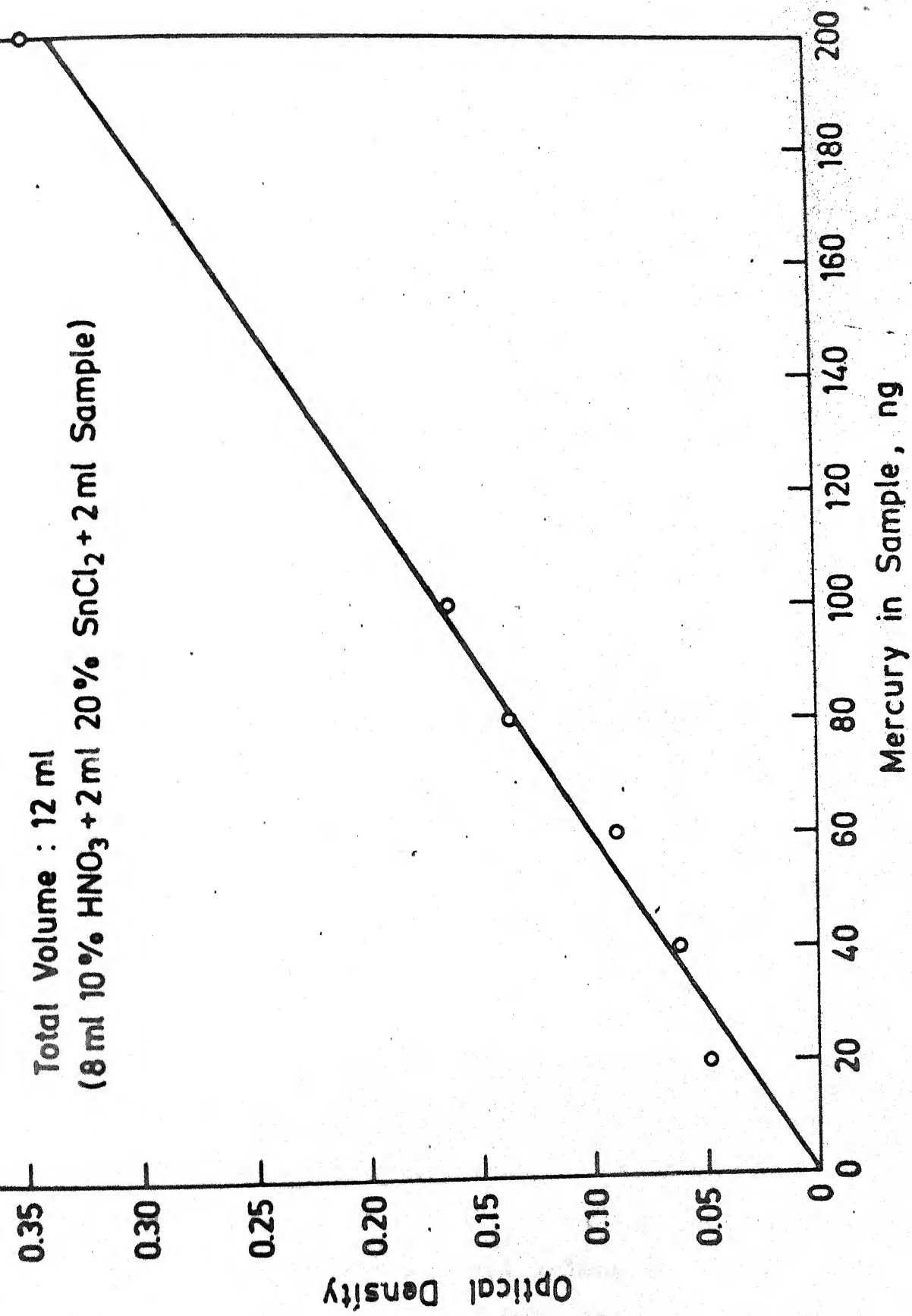


Fig. 4. Calibration Curve for Estimation of Mercury.

of the experiment. This study was conducted to determine the equilibrium time.

Batch isothermal studies were conducted with different initial mercury concentrations and 500 mg/l sorbent using the time required to obtain equilibrium as determined in the kinetic studies. Batch isothermal studies were conducted to estimate the sorption capacity and sorption intensity of the sorbents under consideration.

Using the time required to obtain equilibrium, sorption tests were conducted to evaluate the effect of pH on mercury sorption. The reaction mixture was adjusted to various initial pH values using nitric acid and sodium hydroxide. The effect of pH on mercury sorption was evaluated for all the sorbents used in the kinetic and isothermal studies.

#### 4.7.2 Desorption and Regeneration Studies

The desorption and regeneration studies were carried out only for those sorbents which showed a good performance in the batch sorption tests, against Filtrasorb-400 as a reference. For desorption studies, 200 mg of sorbent was loaded with mercury using 200 ml of a 100 mg/l solution and a contact time of 12 h. Experimental conditions were similar to that of batch sorption tests. The amount of mercury sorbed was determined by measuring the concentration of mercury remaining in solution. The mercury-loaded sorbent was then filtered through a Whatman-42 filter paper and the retained sorbent was washed gently with glass-distilled water to remove any unsorbed mercury,



followed by air drying. Mercury was then allowed to desorb by suspending in 200 ml of glass-distilled water with agitation. Similar to the sorption kinetic experiments, several identical bottles each containing 200 mg of mercury-loaded sorbent were employed and at various time intervals bottles were withdrawn from the shaker and analysed for desorbed mercury.

For sorbent regeneration studies, the procedure followed for the desorption studies for mercury loading was adopted. Using the equilibrium time determined in desorption kinetic studies, 200 mg of air-dried mercury-loaded sorbent was subjected to 200 ml of regenerant solution with agitation. The mercury desorbed was determined. The sorbent was then filtered through a Whatman No. 42 filter paper, air dried and subjected to another mercury loading cycle. The loading and regenerating cycle was repeated four times. Two regenerants 0.2 N NaCl and 0.1 N HCl, were used in the present study. Pandey (1978) observed 0.2 N NaCl to be an effective regenerant for coal-mercury system. Hydrochloric acid is a common regenerant for ion exchangers.

## 5. RESULTS AND DISCUSSION

The experimental work was divided into four phases to facilitate the presentation of the data. The results are presented either in graphical or tabular form depending on convenience. A discussion of the results follows each phase of the experimental work.

### 5.1 Sorption Kinetics

Evaluation of the suitability of sorption as a unit operation requires the consideration of two important physicochemical aspects of the process, the kinetics and the equilibria of sorption. Kinetics of sorption describing the solute uptake rate, which in turn governs the contact time is one of the important characteristics defining the efficiency of sorption. The study of the equilibrium established in any liquid-solid system is important in determining the distribution of the solute between the solid and liquid phases, and in determining the feasibility and capacity of the sorbent for sorption. The rate at which sorption proceeds is important in terms of the contact time to be provided between the solution and the sorbent. The capacity of the sorbent for the uptake of sorbate, i.e., the position at which equilibrium is attained determines the useful life of sorbent to a large extent.

Figure 5 shows the uptake of mercury by Filtrasorb-400, GBC and the other four impregnated coal sorbents as a function of time. In general, the time required to attain

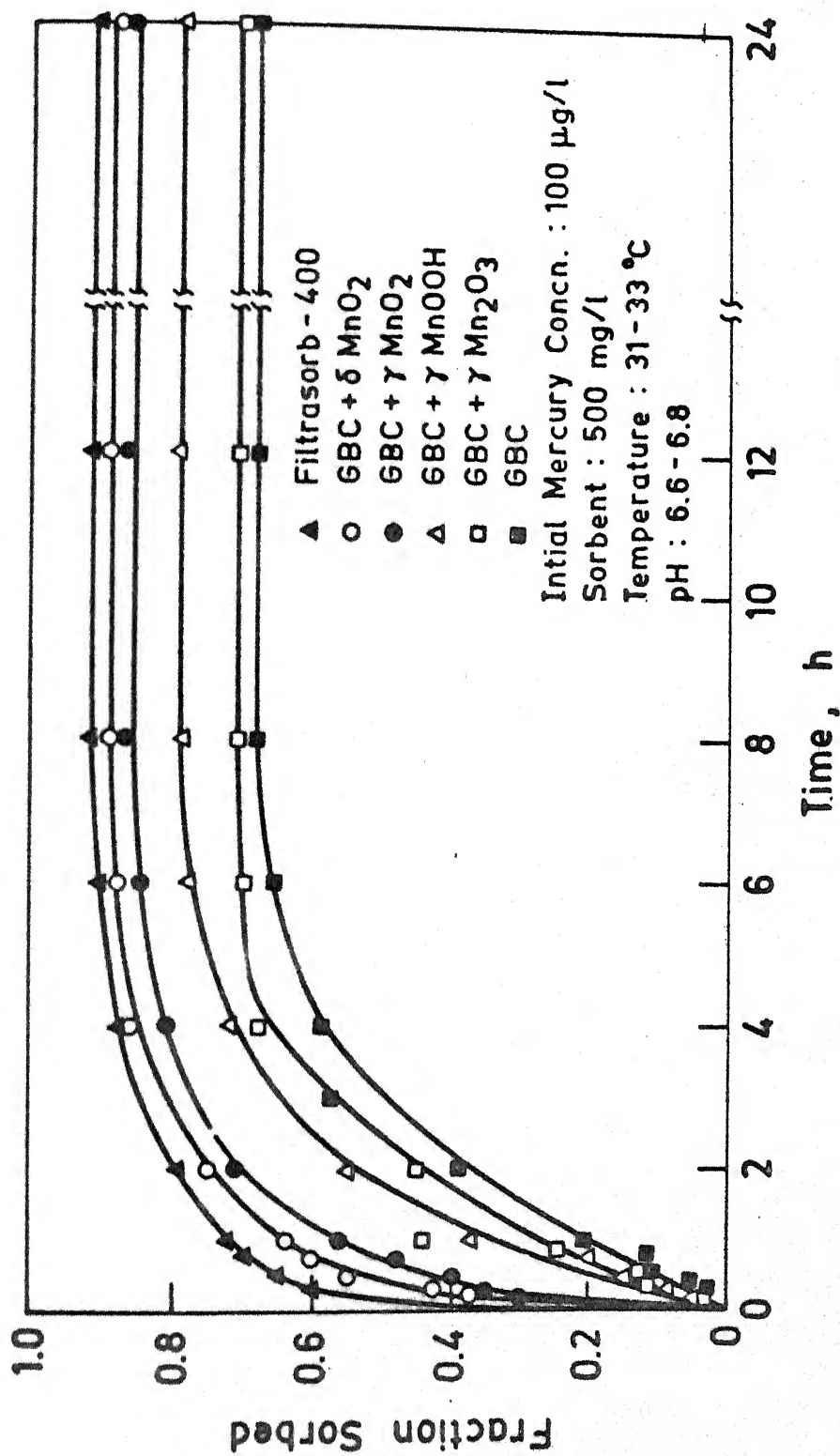


Fig. 5. Sorption Kinetics of Mercury .

equilibrium for all sorbents was 8-10 h. In all subsequent sorption experiments an equilibrium time of 12 h was employed. Among the impregnated sorbents  $\delta\text{MnO}_2$  impregnated and  $\gamma\text{MnO}_2$  impregnated coal showed a very high uptake rate and sorption capacity which compared well with those of Filtrasorb-400. The initial high uptake rates decreased gradually as the equilibrium approached.  $\gamma\text{MnOOH}$  impregnated coal though did not show a very high uptake rate and sorption capacity, exhibited a significant improvement over the untreated coal. But, the  $\gamma\text{Mn}_2\text{O}_3$  impregnated coal did not show significant improvement either in terms of uptake rate or sorption capacity.

The sorption of mercury from liquid phase to solid phase may be considered as a reversible reaction with an equilibrium being established between the two phases. A simple first order reversible kinetic model was used to establish the rates of reaction which can be expressed as



If the first order reversible kinetic model holds good, the rate equation for the reaction may be expressed as

$$\begin{aligned} \frac{dC_B}{dt} &= -\frac{dC_A}{dt} = C_{A_0} \frac{dx_A}{dt} = k_1 C_A - k_2 C_B \\ &= k_1 (C_{A_0} - C_{A_0} x_A) - k_2 (C_{B_0} + C_{A_0} x_A) \end{aligned} \quad (11)$$

where  $C_A$  and  $C_B$  are the concentrations of mercury in solution and on sorbent at any time respectively,  $C_{A_0}$  and  $C_{B_0}$

$$\text{where } k' = K_1 \left(1 + \frac{1}{K_c}\right) = k_1 + k_2 \quad (17)$$

and

$$U(t) = \frac{C_{A_0} - C_A}{C_{A_0} - C_{A_e}} = \frac{x_A}{x_{A_e}} \quad (18)$$

$k'$  is the first order overall rate constant and  $U(t)$  represents the fractional attainment of equilibrium (Helfferich, 1962).

Figure 6 is a plot of the sorption kinetic data according to equation (16). Sorption kinetic data of all the sorbents gave a straight line fit justifying the validity of the assumption, the sorption data follow first order reversible kinetics. From the first order reversible kinetic fit of the sorption data it may also be noted that the straight lines did not pass through the origin in case of  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  impregnated coal sorbents, and Filtrasorb-400 indicating an initial high rate of mercury uptake during the first few minutes. This was probably due to some active sites existing on the surface of the sorbents having high affinity for mercury as observed by Michelsen et al. (1975) in mercury-hair system. They evaluated the slopes after the initial drop.

The values of  $k'$  were evaluated from the slopes of the first order reversible kinetic plots.  $K_c$ ,  $k_1$  and  $k_2$  were evaluated using equations (13) and (17). The values are shown in Table 9. The calculated  $k'$  values for  $\gamma\text{MnOOH}$  and  $\gamma\text{Mn}_2\text{O}_3$  impregnated coal sorbents, and coal confirm the

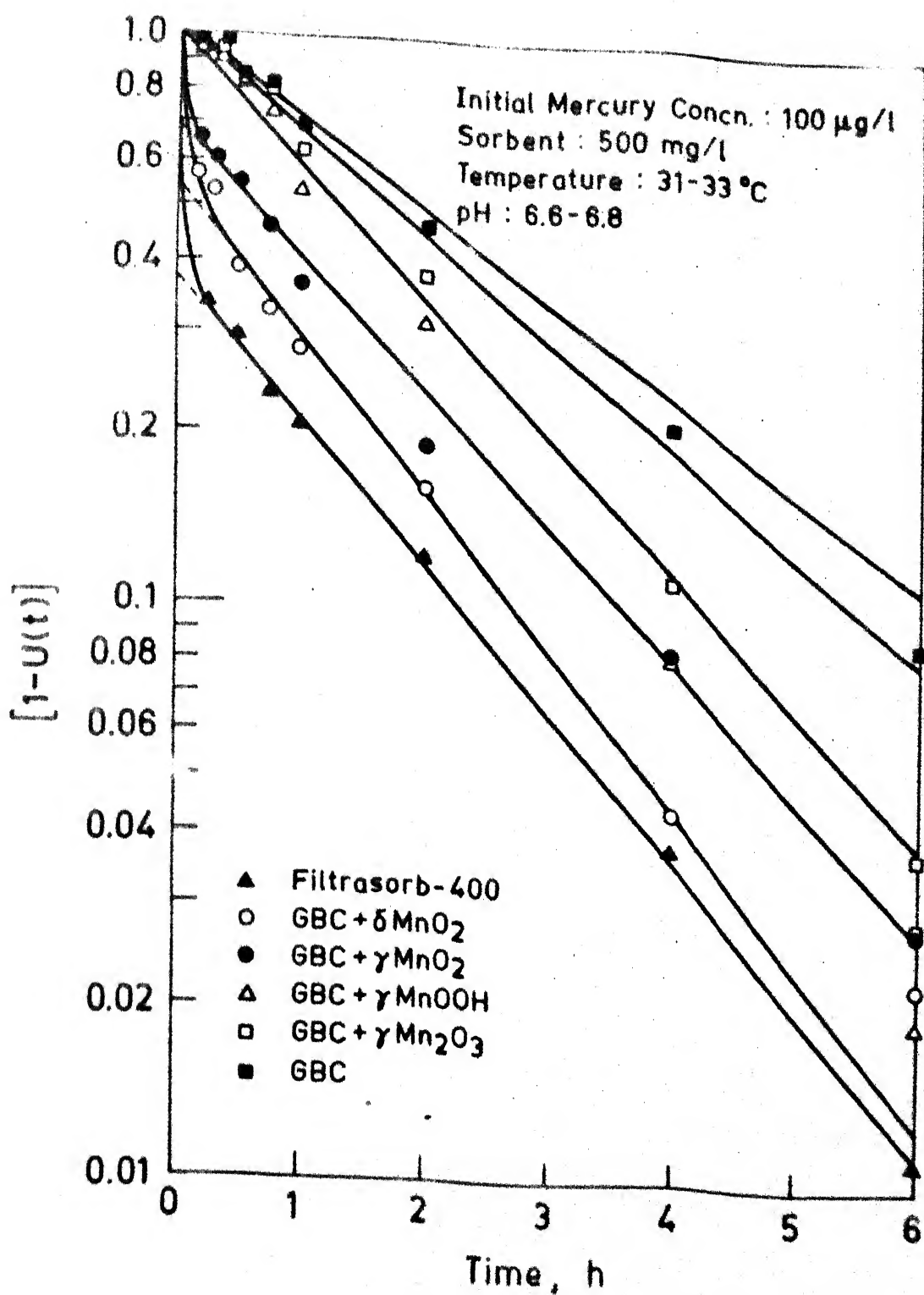


Fig. 6 First Order Reversible Kinetic Fit of Mercury Sorption Data.

observations made based on Figure 5, i.e., the rate of uptake of mercury in the ascending order is as follows: GBC,  $\gamma\text{Mn}_2\text{O}_3$  impregnated coal,  $\gamma\text{MnOOH}$  impregnated coal. An idea about the suitability for desorption can be had from the  $k_2$  values since it represents the rate of sorbate transfer from sorbent to solution. The suitability for desorption of these sorbents may follow the following order:  $\text{GBC} > \gamma\text{Mn}_2\text{O}_3$  impregnated coal  $> \gamma\text{MnOOH}$  impregnated coal since the  $k_2$  values decreased in this order. The values of  $k'$  cannot be used in case of  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  impregnated coal sorbents and Filtrasorb-400 to confirm the overall rate because the straight lines of first order kinetic fit did not pass through the origin when extended. This idea can be confirmed by comparing  $k'$  values calculated from Figure 6 and the uptake rate observed from Figure 5. For example,  $k'$  value for Filtrasorb-400 should have been the highest since it showed the highest rate of uptake of mercury (Figure 5) which is not so. Hence, an idea about desorption also cannot be had from  $k_2$  values for it was calculated using  $k'$  values. But, an idea about desorption can be had from  $\frac{1}{K_c}$  values. The suitability of these sorbents in view of desorption may follow the following order:  $\gamma\text{MnO}_2$  impregnated coal  $> \delta\text{MnO}_2$  impregnated coal  $> \text{Filtrasorb-400}$ . This prediction was found to be correct when desorption experiments were conducted.

First order reversible kinetic plots were used to have an idea about the rate limiting step. The straight line portions showed in Figure 6 were used to evaluate  $t_{1/2}$ ,

time required to sorb 50 percent of the amount sorbed at equilibrium. According to Helfferich (1962), the pore diffusion coefficient ( $\bar{D}$ ) and the film diffusion coefficient ( $D$ ) can be calculated from the following equations.

$$t_{1/2} = 0.03 \frac{r_o^2}{\bar{D}} \quad (19)$$

$$t_{1/2} = 0.23 \frac{r_o \delta \bar{C}}{D C} \quad (20)$$

where  $r_o$  is the radius of the sorbent (cm),  $\bar{D}$  is the pore diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $D$  is the film diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $\frac{\bar{C}}{C}$  is the equilibrium loading of the sorbent which is equal to  $(C_o - C_e)/C_e$  where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of sorbate in solution respectively and  $\delta$  is the film thickness (cm).

Assuming spherical geometry for the sorbents, thickness of the film as  $10^{-3}$  cm (Helfferich, 1962) and evaluating  $t_{1/2}$  from Figure 6 (for Filtrasorb-400 it was estimated from Figure 5 since it was not possible to use Figure 6 due to significant initial drop).  $\bar{D}$  and  $D$  were calculated and presented in Table 10.

According to Michelsen et al. (1975), for heavy metal sorption,  $D$  should lie between  $10^{-6}$  and  $10^{-8}$   $\text{cm}^2/\text{s}$  for film diffusion to be rate limiting and  $\bar{D}$  should lie between  $10^{-11}$  and  $10^{-13}$   $\text{cm}^2/\text{s}$  for pore diffusion to be rate limiting. From the values shown in Table 10 it can be said that film diffusion was rate limiting in the experimental system.



Table 9

Values of Rate Constants ( $k'$ ,  $k_1$ ,  $k_2$ ), and  $K_c$  and  $1/K_c$ 

Sorbent	$k'$ per hour	$K_c$	$k_1$ per hour	$k_2$ per hour	$1/K_c$
Filtrisorb-400	0.58	11.5	0.5336	0.0464	0.087
GBC + $\delta\text{MnO}_2$	0.63	8.09	0.56	0.0693	0.1237
GBC + $\gamma\text{MnO}_2$	0.53	6.14	0.456	0.0742	0.1628
GBC + $\gamma\text{MnOOH}$	0.54	4.00	0.432	0.108	0.250
GBC + $\gamma\text{Mn}_2\text{O}_3$	0.41	2.45	0.291	0.119	0.4085
GBC	0.36	2.23	0.248	0.111	0.4494

Table 10

Values of Diffusion Coefficients ( $\bar{D}$  and  $D$ ) for Sorbents

Sorbent	$\bar{D}$ $\text{cm}^2/\text{sec}$	$D$ $\text{cm}^2/\text{sec}$
Filtrisorb-400	$1.88 \times 10^{-8}$	$8.55 \times 10^{-8}$
GBC + $\delta\text{MnO}_2$	$1.56 \times 10^{-8}$	$5.01 \times 10^{-8}$
GBC + $\gamma\text{MnO}_2$	$5.086 \times 10^{-9}$	$1.23 \times 10^{-8}$
GBC + $\gamma\text{MnOOH}$	$2.352 \times 10^{-9}$	$0.372 \times 10^{-8}$
GBC + $\gamma\text{Mn}_2\text{O}_3$	$1.792 \times 10^{-9}$	$0.182 \times 10^{-8}$
GBC	$1.568 \times 10^{-9}$	$0.138 \times 10^{-8}$

The values of fraction sorbed vs. time<sup>1/2</sup> were plotted and shown in Figure 7. The plots are similar for GBC,  $\gamma\text{MnOOH}$  impregnated coal and  $\gamma\text{Mn}_2\text{O}_3$  impregnated coal, consisting of an initial curved portion, a linear portion and a final curved portion. The initial curved portion was absent in case of Filtrasorb-400,  $\delta\text{MnO}_2$  impregnated coal, and  $\gamma\text{MnO}_2$  impregnated coal. According to Alexander et al. (1978), if the sorbent particle is surrounded by a boundary layer (film) through which the sorbate must diffuse before getting adsorbed on external surface, the initial curvature results. The linear portion of the plot is due to pore diffusion being predominant in the rate controlling step. The final curve is because of the decrease in the concentration of mercury as time progresses, which results in a decrease in the rate of diffusion.

It may be mentioned here that a common observation during the sorption experiments was that the pH of the reaction mixture decreased by about one unit following sorption for all the sorbents. This indicated ion exchange reaction in sorption.

## 5.2 Sorption Equilibria

Sorption in any given system proceeds until the concentration of solute (sorbate) remaining in solution is in dynamic equilibrium with that at the surface (sorbent). At this position of equilibrium, there is a defined distribution of solute between the solid and liquid phases. The distribution ratio is a measure of the position of equilibrium in the sorption process. The preferred form for

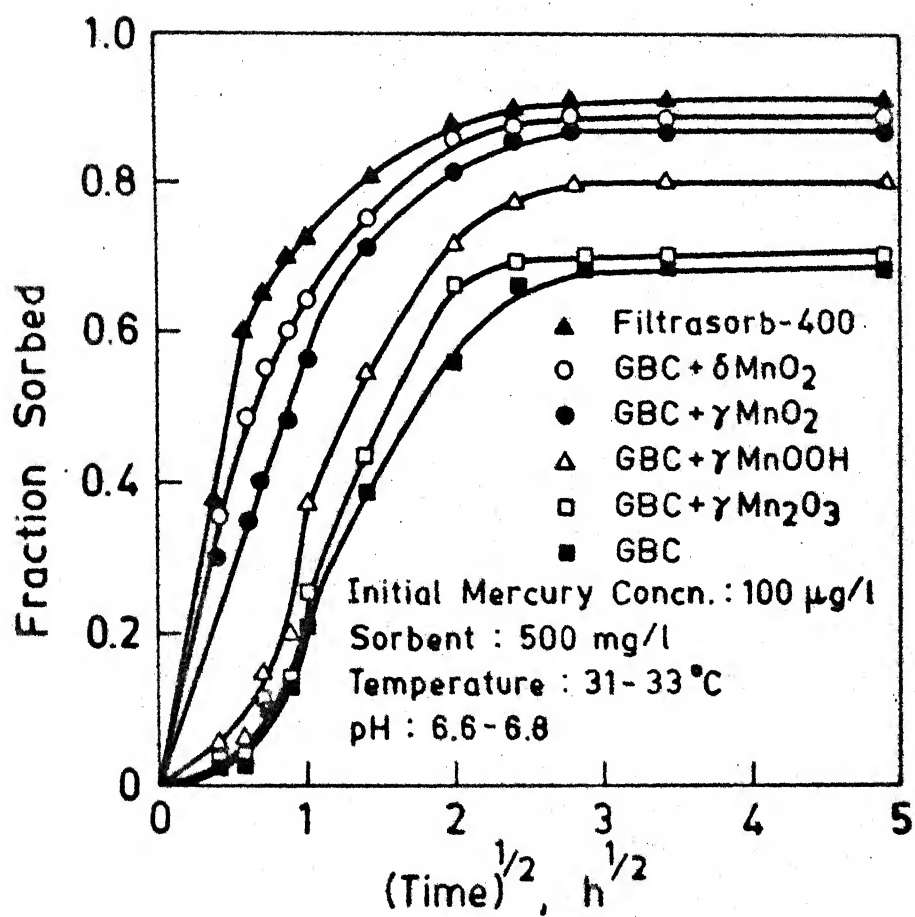


Fig. 7. Mercury Sorbed Against  $(\text{Time})^{1/2}$  for Various Sorbents.

depicting this distribution is to express the amount of solute sorbed per unit weight of sorbent as a function of the concentration of solute remaining in solution under equilibrium at constant temperature. An expression of this type is known as sorption isotherm.

Figure 8 shows the sorption isotherms for mercury sorption used in the present study. The isotherms for Filtrasorb-400, coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  conform to  $L_1$  type of Giles classification of isotherms (Giles, 1970). The isotherms for GBC and coal impregnated with  $\gamma\text{Mn}_2\text{O}_3$  conform to  $L_2$  type and that for coal impregnated with  $\gamma\text{MnOOH}$  falls between  $L_1$  and  $L_2$  types of Giles classification. In general, L type curves reflect the Langmuir's assumption that the intermolecular forces between the sorbent and sorbate would not be significant beyond the first sorbed layer and that a portion of the sorbate molecules adheres, while the remainder rebounds into the liquid phase. The interaction between adjacent molecules on the surface is relatively weak. Presence of solvent over the remainder of the surface simply has the effect of reducing the tendency of a bombarding sorbate molecule to adhere to the sorbent, since it will need additional energy to dislodge solvent molecules before remaining on the surface.  $L_1$  type represents non-completion of monolayer, whereas  $L_2$  represents the completion of monolayer.

Since straight line plots can be more readily extrapolated to concentrations outside the experimental range and interpolated within a range, many investigators present

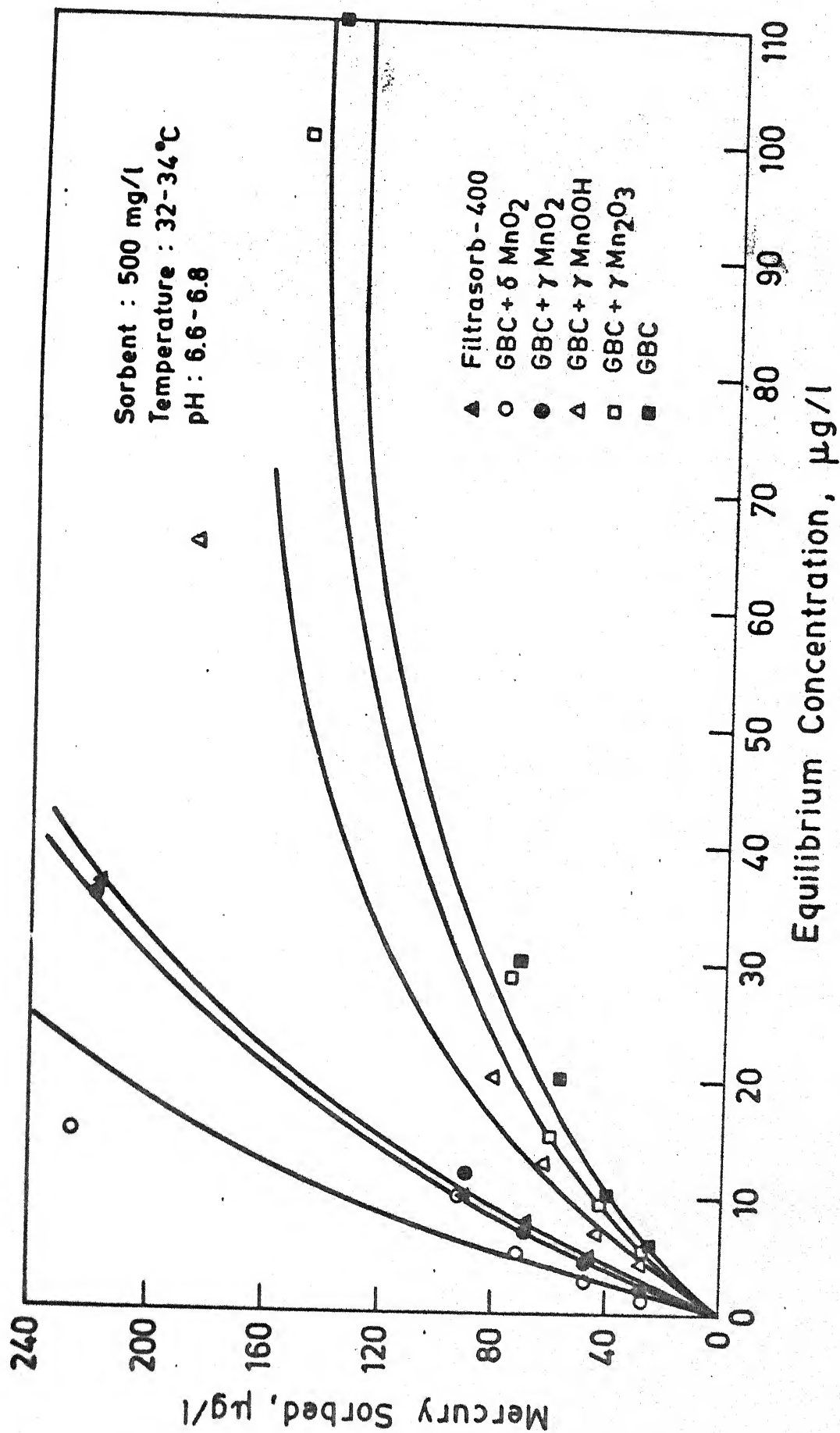


Fig. 8. Isotherms for Mercury Sorption.

isotherms plotted in a manner so as to produce as straight a line as possible. The two primary plotting schemes derive from the Langmuir and Freundlich equations (Neely and Isacoff, 1982).

The Langmuir equation is presented as

$$\frac{x}{m} = \frac{abC}{1 + aC} \quad (21)$$

where,  $x$  = mass of sorbate (mg),  $m$  = mass of dry sorbent (g),  $a$  = constant (1/mg),  $b$  = maximum capacity - assumed to be monolayer coverage of sorbent surface (mg/g) and  $C$  = solution concentration at equilibrium (mg/l). Two convenient linear forms of the Langmuir equation are

$$\frac{m}{x} = \frac{1}{b} + \frac{1}{ab} \left(\frac{1}{C}\right) \quad (22)$$

or

$$\frac{C}{(x/m)} = \frac{1}{ab} + \frac{C}{b} \quad (23)$$

Either of these forms may be used for linearisation of data that accord with Langmuir equation. The form chosen usually depends on the range and spread of the data and on the particular data to be emphasized (Weber, 1972).

The Freundlich equation has the general form

$$\frac{x}{m} = kC^{1/n} \quad (24)$$

where,  $k$  and  $n$  are constants and  $x$ ,  $m$  and  $C$  are defined as in the Langmuir equation.

The linearised form of Freundlich equation is

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \quad (25)$$

A plot of the equation (25) is convenient to determine sorption capacity,  $k$  and the sorption intensity,  $\frac{1}{n}$ .

The choice of the equation used for plotting is determined by which one gives the straightest line. In the present study, coefficient of correlation values were calculated for the sorption equilibria data to fit into linear forms represented by equations (22), (23) and (25).

Table 11 shows the coefficient of correlation values ( $r$ ). The ' $r$ ' values were found to be higher for  $\frac{m}{x}$  versus  $\frac{1}{C}$  than those for  $\frac{C}{(x/m)}$  versus  $C$ . But because of the spread of the data equation (22) could not be plotted. Equation (23) was not chosen for it gave low ' $r$ ' values, e.g., 0.384 for GBC impregnated with  $\delta\text{MnO}_2$ . The ' $r$ ' values for Langmuir isotherm (equation (22)) and Freundlich isotherm (equation (25)) were found to be almost same. Hence, it can be said that sorption equilibria data followed both Langmuir and Freundlich isotherms. Linearised Freundlich isotherms for all the sorbents used in the present study are shown in Figure 9. The sorption capacities for  $C = 1 \mu\text{g/l}$  and sorption intensities obtained from Figure 9 are shown in Table 12. Among the six sorbents used in the present study, GBC impregnated with  $\delta\text{MnO}_2$  exhibited the highest sorption capacity and the highest sorption intensity. The isotherms for GBC impregnated with  $\gamma\text{MnO}_2$ , and Filtrasorb-400 intersected each other showing higher sorption capacity of GBC impregnated with  $\gamma\text{MnO}_2$  at low concentrations and higher capacity of Filtrasorb-400 at high concentrations. ' $k$ ' for GBC impregnated with  $\gamma\text{MnOOH}$  is not much higher than that for GBC,

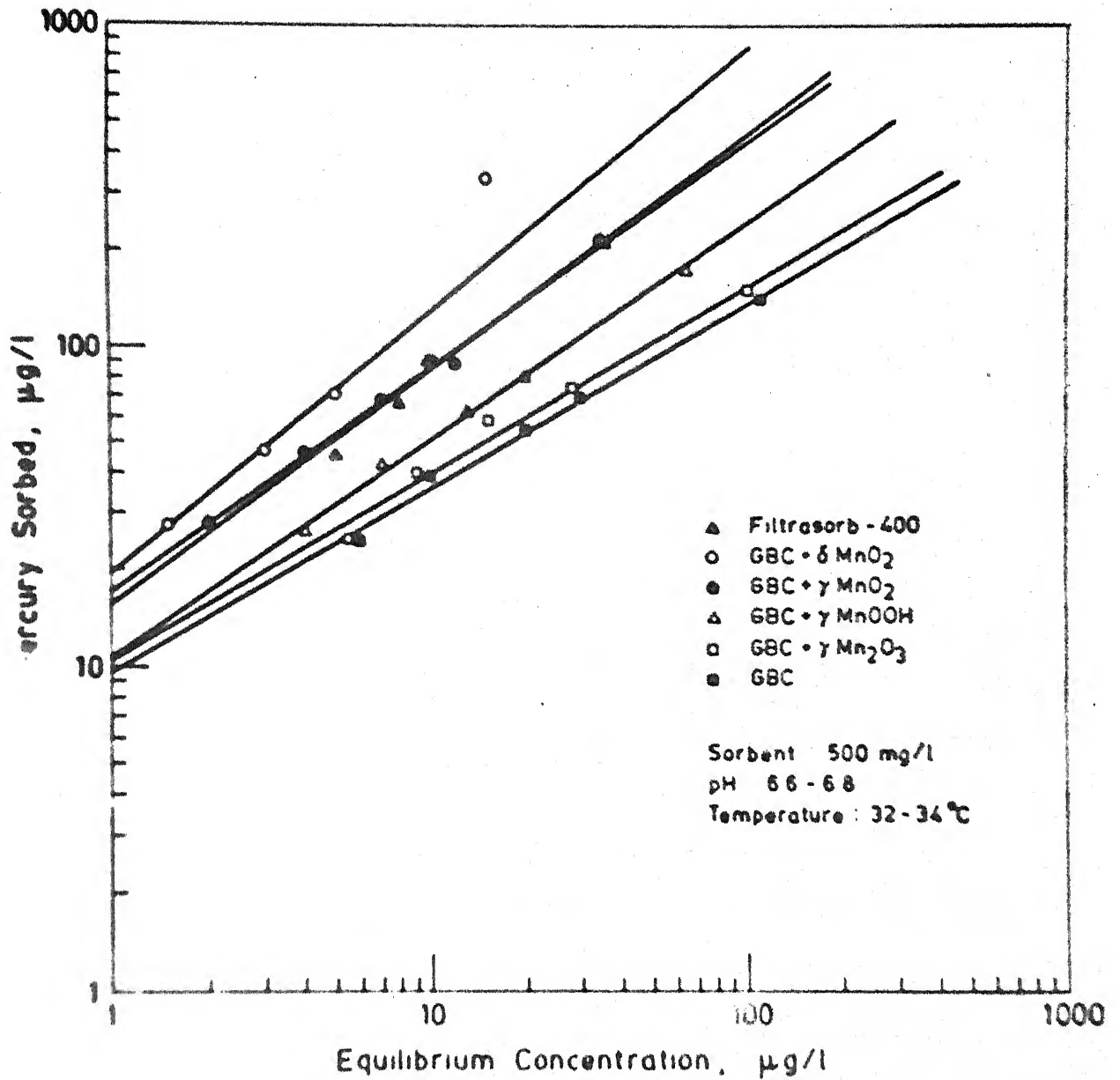


Fig 9 Linearised Freundlich Isotherms



Table 11

Coefficient of Correlation (r) Values for Linearised Isotherms

Sorbent	$\frac{m}{x}$ Vs. $\frac{1}{C}$	$\frac{C}{(x/m)}$ Vs. C	$\log(\frac{x}{m})$ Vs. $\log C$
Filtrisorb-400	0.975	0.917	0.994
GBC + $\delta\text{MnO}_2$	0.985	0.384	0.958
GBC + $\gamma\text{MnO}_2$	0.993	0.914	0.997
GBC + $\gamma\text{MnOOH}$	0.996	0.967	0.998
GBC + $\gamma\text{Mn}_2\text{O}_3$	0.993	0.985	0.984
GBC	0.993	0.989	0.992

Table 12

 $\frac{1}{n}$  and k Values for Various Sorbents

Sorbent	$\frac{1}{n}$	$k$ , $\mu\text{g}/500 \text{ mg}$ (for $C = 1 \mu\text{g}/\text{l}$ )
Filtrisorb-400	0.722	15.79
GBC + $\delta\text{MnO}_2$	0.821	19.07
GBC + $\gamma\text{MnO}_2$	0.699	17.01
GBC + $\gamma\text{MnOOH}$	0.087	10.59
GBC + $\gamma\text{Mn}_2\text{O}_3$	0.590	10.41
GBC	0.583	9.42

but  $\frac{1}{n}$  value for the former is significantly higher than that for the latter. Hence it can be said that the enhancement in sorption capacity for GBC impregnated with  $\gamma\text{MnOOH}$  is significant at high concentrations when compared with GBC. The  $K$  and  $\frac{1}{n}$  values for GBC impregnated with  $\gamma\text{Mn}_2\text{O}_3$  are only slightly more than that for GBC. Hence, it can be said that  $\gamma\text{Mn}_2\text{O}_3$  impregnation did not improve the performance of GBC significantly.

According to Logsdon and Symons (1973), if the slope of Freundlich isotherm is equal to 1, the fraction sorbed will be irrespective of the initial concentration of sorbate ( $C_o$ ). The proof is given below.

For  $n = 1$ , Freundlich isotherm takes the form

$$\frac{x}{m} = kC$$

or  $x = mkC = k_1C$  (since 'm' is constant).

Solving to eliminate  $x$ ,

$$x = C_o - C = k_1C$$

$$\therefore \frac{C_o}{C} = k_1 + 1$$

inverting

$$\frac{C}{C_o} = \frac{1}{k_1 + 1}$$

Because the percentage removal efficiency is  $(1 - \frac{C}{C_o}) \times 100$  substituting  $\frac{C}{C_o} = \frac{1}{k_1 + 1}$ , percentage removal efficiency is equal to  $(1 - \frac{1}{k_1 + 1}) \times 100$  which is a constant irrespective of initial concentrations for the conditions specified.

Taking a cue from this, a qualitative statement can be made whether the fraction sorbed increases or decreases with increase in initial concentrations (assuming that the isotherm data can be extrapolated). Since  $\frac{1}{n}$  values for all the sorbents used in the present study were found to be less than 1, it can be said that fraction sorbed decreases for all the sorbents with increase in initial concentration. This effect was found to increase in the order of coal impregnated with  $\delta\text{MnO}_2$ , Filtrasorb-400, coal impregnated with  $\gamma\text{MnO}_2$ , coal impregnated with  $\gamma\text{MnOOH}$ , coal impregnated with  $\gamma\text{Mn}_2\text{O}_3$  and GBC.

### 5.3 Effect of pH on Sorption

Effect of pH on mercury sorption is shown in Figure 10. The initial pH values were adjusted with 1 N nitric acid and 1 N sodium hydroxide as required. It is evident from Figure 10 that mercury sorption increased with increase in pH for all the coal sorbents. The rate of increase was very rapid initially and remained fairly constant afterwards. For Filtrasorb-400, fraction sorbed decreased remarkably with increase in pH beyond 7.

Sorption behaviour of cationic metal ions is similar to metal ion hydrolysis and is characterised by a steep pH-sorption edge (Figure 10). The sorption edge is a narrow pH region, often about 2 pH units wide, in which partitioning of metal changes with increasing pH from nearly all in the solution phase to nearly all sorbed, provided sufficient sorption sites and/or sorbent area are available. The reaction is generally accompanied by release of protons

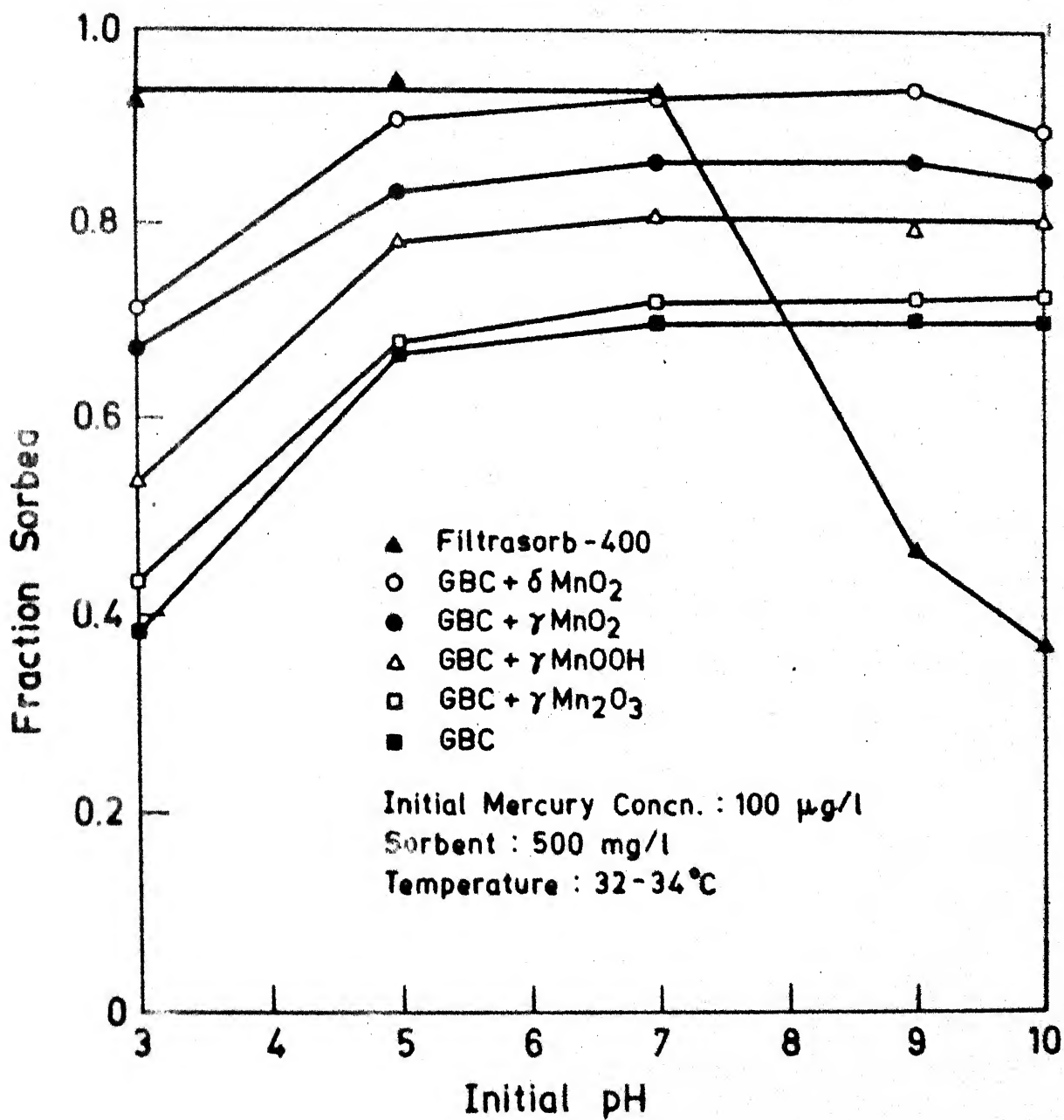


Fig. 10. Effect of pH on Mercury Sorption.

to solution, either by ion-exchange at the surface or by hydrolysis occurring simultaneously with sorption (Hohl and Stumm, 1976; and Benjamin and Leckie, 1981)..

In the present system the mercury species around pH 3 are predominantly  $\text{Hg}^{2+}$ ,  $\text{HgCl}^+$  and  $\text{HgCl}_2^0$ , the molar ratio of chloride to mercury being two. Predominance of the cationic species decreases at higher pH. Since, total chloride concentration is  $10^{-6}$  M  $\text{Hg}(\text{OH})_2^0$  becomes predominant at a pH about 5. At pH 5 besides  $\text{Hg}(\text{OH})_2^0$ ,  $\text{HgCl}_2^0$  and  $\text{HgOHCl}^0$  also will be present. As the pH increases, chloride ions cannot compete with hydroxyl ions. Hence, the formation of  $\text{Hg}(\text{II})\text{-Cl}^-$  complexes decreases. At pH 7  $\text{Hg}(\text{OH})_2^0$  and  $\text{HgOHCl}^0$  will be the dominant species. At pH values 9 and 10 only  $\text{Hg}(\text{OH})_2^0$  will be predominant. These observations are based on Figures 1 and 2.

The effect of pH on mercury sorption by the coal sorbents is explained on the basis of mercury species present in the system and the nature of net surface charge of the sorbent, at a particular pH. For all coal sorbents, mercury sorption was observed to be minimum at pH 3 which was due to the presence of cationic mercury species that could not be readily sorbed because of the net surface charge of all the sorbents was positive ( $\text{pH} < \text{pH}_{\text{zpc}}$ ) at that pH. Besides this, a higher concentration of  $\text{H}^+$  ions present in the reaction mixture which competed with the cationic mercury species for the sorption sites was responsible for low mercury sorption at pH 3. At pH 5, a rapid increase in mercury sorption was observed which was because of the dominance of

$\text{Hg}(\text{OH})_2^0$  species over  $\text{HgCl}_2^0$  and  $\text{HgOHCl}^0$ . A slight increase in mercury sorption was observed at pH 7 over that at pH 5. Since the concentration of  $\text{Hg}(\text{II})\text{-Cl}^-$  complex species decreased which were weakly adsorbable compared  $\text{Hg}(\text{OH})_2^0$ , this is justified. In the pH range 7-10, the fraction sorbed was almost constant, excepting a slight decrease at pH 10 for coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$ , since  $\text{Hg}(\text{OH})_2^0$  was the only dominant species present. At pH 10, the reaction mixture attained a yellowish brown colour when the sorbents used were coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$ , which was observed over the entire pH range studied (3-10) in case of coal impregnated with  $\gamma\text{Mn}_2\text{O}_3$ . Threshold colour numbers were found to be 5, 3 and 2 for coal impregnated with  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$  and  $\gamma\text{Mn}_2\text{O}_3$ , respectively at pH 10. The colour discharged was presumably due to leaching of the oxides of manganese which, in turn, resulted in decreased mercury sorption.

For Filtrasorb-400, the fraction sorbed, decreased remarkably with increase in pH beyond 7. Karthikeyan (1982) also observed a rapid decrease in mercury sorption capacity of Filtrasorb-400 beyond pH 6. Huang and Blackenship (1984) probed into the mechanism of mercury sorption by various activated carbons. According to them, the mechanisms for  $\text{Hg}(\text{II})$  removal are adsorption of mercuric ions at the surface containing both the micro and macropores, and the reduction of the mercuric ions to elemental mercury. The reduction of mercuric ions was found to be accomplished by organic functional groups, such as phenolic, lactone, carboxyl, quinone present on the activated carbon surface

which are good reducing agents. The kinetics of  $\text{Hg(II)}$  adsorption proceeds more rapidly in the acidic pH region and high  $\text{Hg(II)}$  concentration. As the reaction time prolongs, the extent of adsorption reaction decreases and eventually becomes overwhelmed by reduction reaction. Their studies also indicated that the extent of reduction reaction in Filtrasorb-400 was greater in the acidic pH region. Hence, there is a rapid decrease in sorption beyond pH 7.

The effect of pH on mercury sorption demonstrated the suitability of the impregnated coal sorbents in the pH range of natural waters. Among the four impregnated coal sorbents only coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  were tested for regeneration because of their higher efficiency over the other two.

#### 5.4 Desorption and Regeneration

Desorption of mercury-loaded coal sorbents impregnated with  $\delta\text{MnO}_2$ , and  $\gamma\text{MnO}_2$  was carried out using glass-distilled water against Filtrasorb-400 as a reference. The kinetics of mercury desorption are presented in Figure 11. Similar to the sorption kinetics data, desorption data also exhibited a first order reversible kinetic fit (Figure 12). However, it is observed that the overall rate of desorption was lower and the equilibrium was attained in 24 h. Desorption of mercury at equilibrium was 15, 12 and 10 percent of the loadings for  $\delta\text{MnO}_2$  impregnated coal,  $\gamma\text{MnO}_2$  impregnated coal and Filtrasorb-400, respectively. Low desorption of mercury from loaded sorbents in glass-distilled water system was presumably due to release of loosely bound mercury. It further

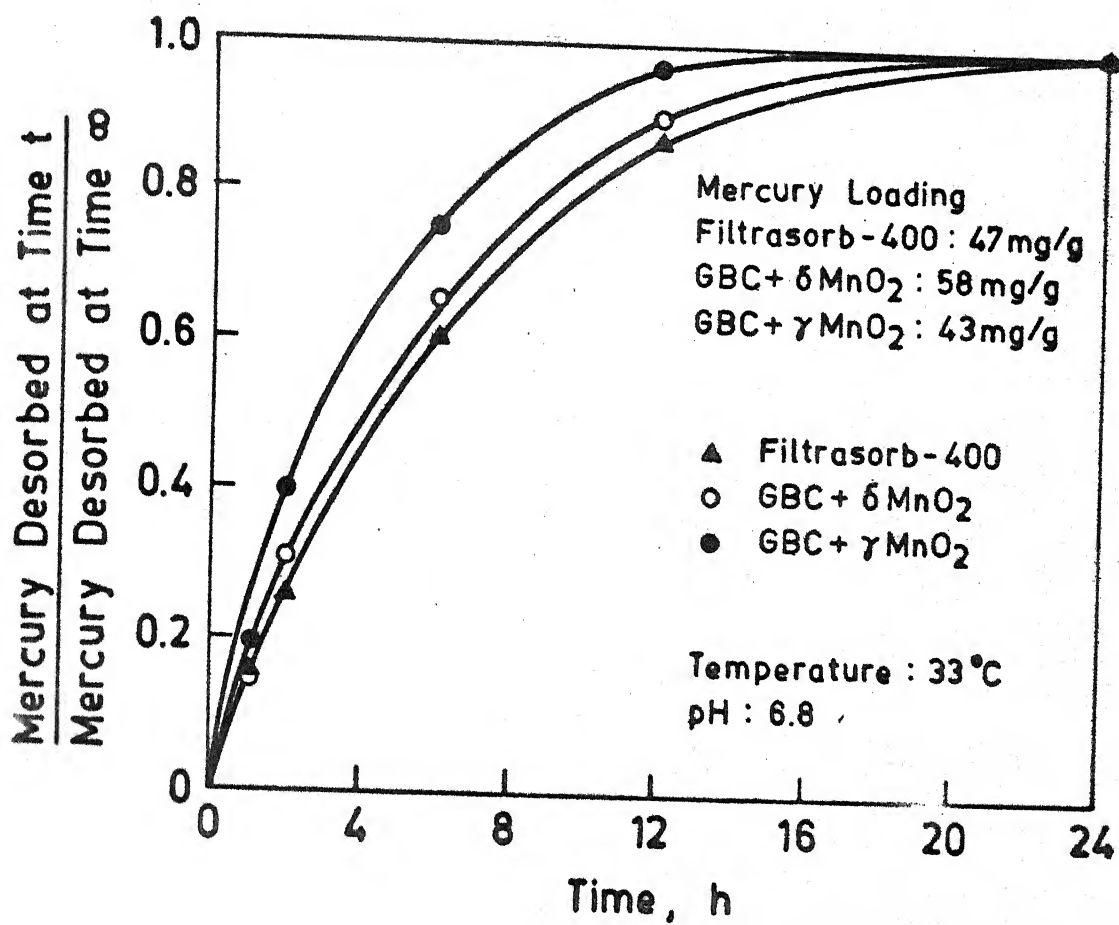


Fig. 11. Desorption of Mercury from Loaded Sorbents.



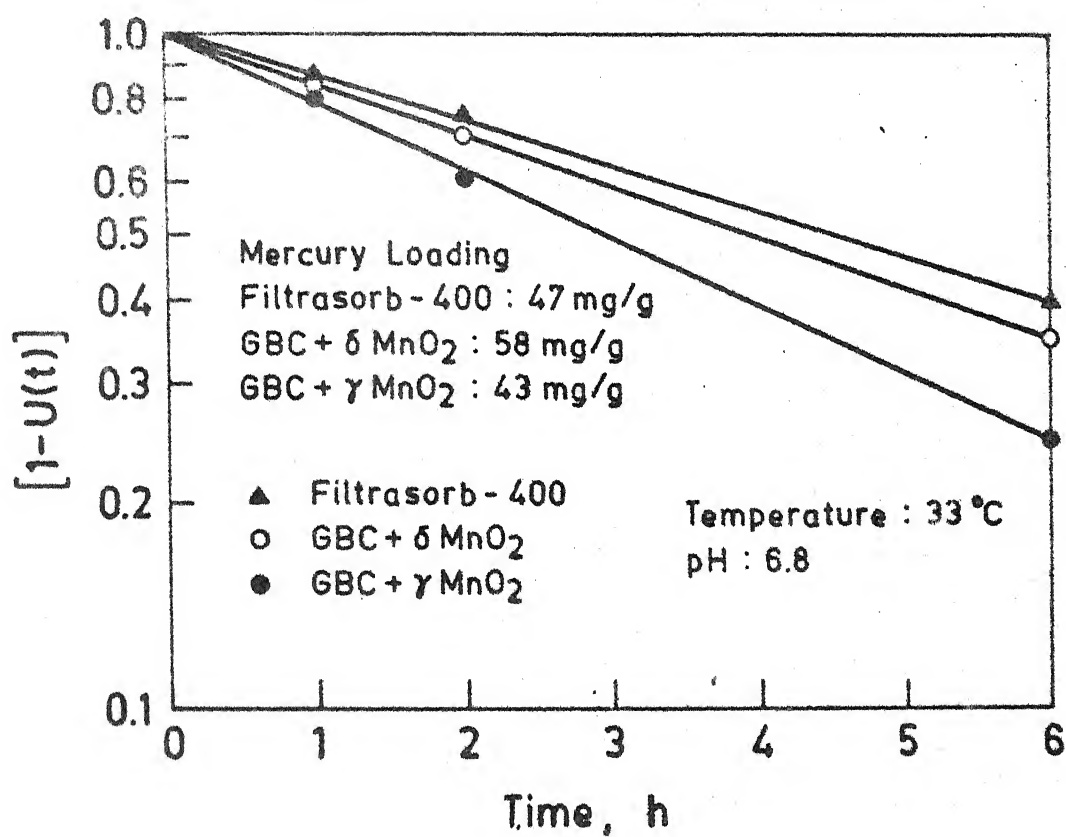


Fig. 12. First Order Reversible Kinetic Fit of Mercury Desorption Data.

indicates the possibility that a major fraction of the sorbed mercury was bound to the sorbents through strongly interactions since the desorption study was conducted at pH 6.8 which was above the  $pH_{zpc}$  of all the sorbents. So, the fraction of mercury which was not desorbed in glass-distilled water system represented the fraction which was sorbed due to exchange sorption. This was further supported by the decrease of pH observed after sorption (Section 5.1).

Regeneration of mercury-loaded coal sorbents impregnated with  $\delta MnO_2$ , and  $\gamma MnO_2$  was carried out using 0.1 N HCl and 0.2 N NaCl, against Filtrasorb-400 as a reference to compare the regeneration efficiency of the impregnated coal sorbents. The regeneration data are shown in Tables 13, 14 and 15. A careful comparison of the regeneration data indicates that 0.2 N NaCl is a better regenerant than 0.1N HCl. A similar observation was made by Pandey (1978) in coal-mercury system. The percent recovery of mercury was found to be more for  $\delta MnO_2$  impregnated coal and  $\gamma MnO_2$  impregnated coal when compared with Filtrasorb-400. The percent loading capacity lost was found to be less for the impregnated sorbents when compared with Filtrasorb-400. A comparison of regeneration data of  $\delta MnO_2$  impregnated coal and  $\gamma MnO_2$  impregnated coal indicates that the percent loading capacity lost was more for the latter sorbent, but the percent recovery of mercury was almost same for both the sorbents. The observation that exchange sorption was operative is well supported by the percent recovery of mercury which is in the range of 70-95 percent when sodium chloride and

Table 13

## Material Balance Calculations for Regeneration of Filtrasorb-400

Type of regenerant	0.1 N HCl				0.2 N NaCl			
	Number of cycles				Number of cycles			
	1	2	3	4	1	2	3	4
Amount of mercury in sorbent from previous recovery cycle (mg mercury/g sorbent)	0.0	9.5	10.0	11.2	0.0	8.5	9.2	9.3
Amount of mercury picked up by sorbent in loading cycle (mg mercury/g sorbent)	47	36.6	34.5	31.6	47	37.5	35.3	35.0
Total amount of mercury going into recovery cycle (mg mercury/g sorbent)	47	46.1	44.5	42.8	47	46	44.5	44.3
Percent loading capacity lost (%)	0	2	5.3	8.9	0	2.1	5.3	5.7
Amount of mercury recovered from sorbent in recovery cycle (mg mercury/g sorbent)	37.5	36.1	33.3	29.9	38.5	36.8	35.2	35.0
Amount of mercury remaining on sorbent (mg mercury/g sorbent)	9.5	10.0	11.2	12.9	8.5	9.2	9.3	9.3
Percent recovery of mercury from sorbent (%)	80	78.5	75	70	82	80	79	79

Table 14

Material Balance Calculations for Regeneration of Coal Impregnated with  $\delta\text{MnO}_2$ 

Type of regenerant	0.1 N HCl				0.2 N NaCl			
	Number of cycles				Number of cycles			
	1	2	3	4	1	2	3	4
Amount of mercury in sorbent from previous recovery cycle (mg mercury/g sorbent)	0	5.5	6.8	8.8	0	3.6	5.2	5.7
Amount of mercury picked up by sorbent in loading cycle (mg mercury/g sorbent)	58.6	52	50	46.9	58.6	54.5	51.8	51.3
Total amount of mercury going into recovery cycle (mg mercury/g sorbent)	58.6	57.5	56.8	55.7	58.6	57.9	57.0	57.0
Percent loading capacity lost (%)	0	1.5	3.0	5.0	0	1.1	2.7	2.7
Amount of mercury recovered from sorbent in recovery cycle (mg mercury/g sorbent)	53.1	50.7	48	44.6	55	52.7	51.3	49.6
Amount of mercury remaining on sorbent (mg mercury/g sorbent)	5.5	6.8	8.8	11.1	3.6	5.2	5.7	7.4
Percent recovery of mercury from sorbent (%)	90.6	88.2	84.5	80.0	93.9	91.0	90	87

Table 15

Material Balance Calculations for Regeneration of Coal Impregnated with  $\text{Ymno}_2$ 

Type of regenerant	0.1 N HCl				0.2 N NaCl			
	Number of cycles				Number of cycles			
	1	2	3	4	1	2	3	4
Amount of mercury in sorbent from previous recovery cycle (mg mercury/g sorbent)	0	3.8	5.6	6.6	0	3.1	3.7	4.0
Amount of mercury picked up by sorbent in loading cycle (mg mercury/g sorbent)	42.6	37.0	33.1	30.5	42.6	38.9	36.8	36.1
Total amount of mercury going into recovery cycle (mg mercury/g sorbent)	42.6	40.8	38.7	37.1	42.6	42.0	40.5	40.1
Percent loading capacity lost (%)	0	4.2	9.1	8.7	0	1.4	4.9	5.8
Amount of mercury recovered from sorbent in recovery cycle (mg mercury/g sorbent)	38.8	35.2	32.1	39.7	39.5	38.3	36.5	35.3
Amount of mercury remaining on sorbent (mg mercury/g sorbent)	3.8	5.6	6.6	7.4	3.1	3.7	4.0	4.8
Percent recovery of mercury from sorbent (%)	91	86.2	83	80	92.7	91.1	90	88

hydrochloric acid were used as regenerants. Significant recovery during regeneration also demonstrates the reversible nature of the sorption reaction. The fraction of the sorbed mercury not recovered during regeneration presumably represents the mercury bound possibly through chemisorption.

Low percent loading capacity lost (3-9 percent) and high percent recovery of mercury (80-88 percent) indicate usefulness of  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  impregnated coal for mercury sorption from a practical viewpoint.

## 6. SUMMARY AND CONCLUSIONS

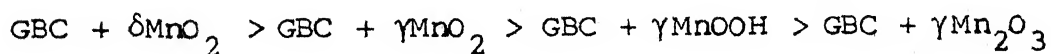
The present study demonstrated the usefulness of impregnation of oxides of manganese, viz.,  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$ ,  $\gamma\text{MnOOH}$  and  $\gamma\text{Mn}_2\text{O}_3$ , on coal in enhancing mercury sorption capacity. The batch sorption kinetics were described by a first order reversible reaction. The first order rate constants were calculated using the sorption kinetics data. The pore diffusion and film diffusion coefficients calculated from the half time equations, indicated that film diffusion was rate limiting in the experimental system. However, fraction sorbed versus  $\sqrt{t}$  plot indicated that pore diffusion was rate limiting for GBC impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  whereas, the same plot indicated that film diffusion was rate limiting for a short period and later on pore diffusion was observed to be rate limiting for GBC impregnated with  $\gamma\text{MnOOH}$  and  $\gamma\text{Mn}_2\text{O}_3$ . The release of protons from sorbents during the sorption of mercury indicated that ion exchange mechanism was operative. The sorption equilibria data followed both Langmuir and Freundlich isotherms. Mercury sorption was found to be pH dependent. Mercury sorption increased with increase in pH upto 7 and remained fairly constant thereafter, excepting a slight decrease at pH 10 for coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  which might be due to leaching of the oxides from coal at that pH. Among the four impregnated sorbents used in this study, coal impregnated with  $\delta\text{MnO}_2$  and  $\gamma\text{MnO}_2$  exhibited high sorption capacities and intensities when compared with untreated coal.

Coal impregnated with  $\delta\text{MnO}_2$  was found to be more efficient than Filtrasorb-400 whereas, coal impregnated with  $\gamma\text{MnO}_2$  was found to be more efficient than Filtrasorb-400 in low mercury concentrations and slightly less efficient in high mercury concentrations.  $\gamma\text{MnOOH}$  impregnation exhibited significant enhancement in mercury sorption capacity at high concentrations studied in the present investigation.  $\gamma\text{Mn}_2\text{O}_3$  impregnation did not enhance the mercury sorption capacity significantly.

Desorption studies indicated an exchange sorption mechanism apart from possible contribution due to chemisorption. Regeneration studies indicated that 0.2 N NaCl is a better regenerant than 0.1 N HCl. Low percent loading capacity lost indicated long life of the sorbents.

Based on the findings of this investigation the following conclusions may be drawn:

1. Impregnation of  $\delta\text{MnO}_2$ ,  $\gamma\text{MnO}_2$ ,  $\gamma\text{MnOOH}$  or  $\gamma\text{Mn}_2\text{O}_3$  on coal enhances its mercury sorption capacity.
2. The impregnated coals may be ranked in the following order in view of the observed sorption capacity and intensity:



From this it appears that mercury sorption capacity of impregnated coal increases with the increase in oxidation grade of manganese present in the oxide of manganese used for impregnating.



3. Sorption of mercury is dependent on pH of the reaction mixture. In general, mercury sorption increases with increase in pH for the impregnated coal sorbents and coal.
4.  $\delta\text{MnO}_2$  or  $\gamma\text{MnO}_2$  impregnated coal is a useful sorbent for mercury in the pH range of natural water and 0.2 N sodium chloride is an effective regenerant for GBC +  $\delta\text{MnO}_2$  and GBC +  $\gamma\text{MnO}_2$ .
5. Mercury sorption may be accounted for mainly by exchange sorption apart from the possible contribution due to chemisorption.

## 7. SIGNIFICANCE OF THE STUDY AND SUGGESTIONS FOR FUTURE WORK

The present investigation has indicated that the impregnation of  $\delta\text{MnO}_2$  or  $\gamma\text{MnO}_2$  on coal enhances the mercury sorption capacity to a level greater than that of activated carbon (Filtrisorb-400). The impregnated sorbents are useful in the pH range of natural water. Such sorbents would be very much welcome in many developing countries where good quality of activated carbon is expensive.

Attempts should continue to develop alternates to activated carbon. As it has been established in the present study that the impregnation of  $\delta\text{MnO}_2$  or  $\gamma\text{MnO}_2$  enhances the sorption capacity of coal, attempts may be made to enhance the sorption capacity of other locally available low cost materials through impregnation of these oxides. Optimisation of impregnation technique is essential in terms of minimising the cost of preparation without loss of efficiency. To understand the sorption mechanism, an intensive characterisation of the impregnated sorbents should be done, for example, determination of oxidation grade of manganese present on the surface of the coal.

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